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INFLUENCE OF SOME NON-LINEAR EFFECTS ON THE MASS TRANSFER KINETICS IN FALLING LIQUID FILMS

CHR. BOYADJIEV
Central Laboratory of Chemical Engineering, Bulgarian Academy of Sciences, 1040, Sofia, Bulgaria

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Abstract—A non-linear theory of mass transfer phenomena in falling liquid films in the presence of gas absorption and fast chemical reaction in the film is presented. A perturbation theory investigation has been carried out to study the influence of high concentration gradients due to a very thin diffusion boundary layer in the film with chemical reaction. The existence of second kind non-linear effects resulting from the high concentration gradients has been shown and quantitative estimates of their influence on the mass transfer rate have been derived.

NOMENCLATURE

- A dimensionless number
- c molar concentration of the substance
- c^* equilibrium concentration
- C dimensionless concentration
- D diffusion coefficient
- D_0 diffusion coefficient of the absorbent
- $\bar{D}$ dimensionless parameter
- Da Damköller's number
- Fo Fourier number
- g gravitational constant
- h film thickness
- h_0 initial film thickness
- H dimensionless film thickness
- I total flux of the absorbed substance through the interface
- J rate of mass transfer
- k rate constant of chemical reaction
- M molecular mass of the absorbed substance
- Q_0 initial liquid flow rate of the film
- u x-component of velocity
- $\bar{u}_0$ characteristic velocity
- U X-component of dimensionless velocity
- v y-component of velocity
- V Y-component of dimensionless velocity
- x longitudinal coordinate
- X dimensionless longitudinal coordinate
- y transverse coordinate
- Y dimensionless transverse coordinate.

Greek symbols

- β mass transfer coefficient accounting for non-linear effects
- β_0 mass transfer coefficient not accounting for non-linear effects
- δ diffusion boundary-layer thickness
- $\varepsilon, \varepsilon_0$ small parameters
- η dimensionless variable
- θ, θ_0 small parameters
- μ dynamic viscosity
- $\bar{\mu}$ dimensionless parameter
- ξ dimensionless variable
- ρ density
- ρ_0 density of pure absorbent
- ρ^* density of absorbent with concentration c^*
- $\bar{\rho}$ dimensionless parameter.

Superscripts

- $*$ values of quantities of the film surface
- $'$ ordinary derivative of a function.

1. INTRODUCTION

INTENSIFICATION of industrial absorption processes is often achieved by utilizing absorbents that interact chemically with the gas absorbed. The presence of chemical reaction in the liquid phase results in a very thin diffusion boundary layer in the liquid and the high concentration gradient thus obtained is the reason for the increased rate of the absorption process. For the case under consideration, the high mass flux through the interface might result in momentum transfer of the same magnitude with the one along the film flow; this means that the high concentration gradient induces a secondary flow in the film. Thus, the flow velocity depends on the concentration of the absorbed substance, and non-linearity arises in the convective mass transfer term in the convective diffusion equation. This effect will be referred to as a first kind non-linear effect.

The basic parameters of the absorbent, which determine the hydrodynamics and the mass transfer of the flow, are the density, viscosity and diffusivity. In general, their dependence on the concentration of the absorbed gas is practically negligible, but one might expect that in the presence of high concentration gradients this effect might become substantial. Inserting these functional relations into the equation of motion and convective diffusion leads to the rise of additional non-linear effects that will be referred to in what follows as the second kind non-linear effects.

The aim of this paper is to present a solution to the problem of determining the influence of the chemical reaction rate in the liquid phase on the characteristics of the flow and the mass transfer rate in a falling liquid film, accounting for both the first and the second kind non-linear effects.

2. CONVECTIVE MASS TRANSFER IN A FALLING LIQUID FILM IN THE PRESENCE OF HIGH CONCENTRATION GRADIENTS

The mathematical description of convective mass transfer in the presence of high concentration gradients is developed in a number of papers [1, 2]. For the case of mass transfer in the liquid phase in the presence of gas absorption in a laminar liquid film, where a fast chemical reaction also occurs, it was shown in ref. [3] that the mathematical description might be presented in the zero-order approximation with respect to the parameter h_0/l, which is very small for falling films. Thus, the mathematical model of convective mass transfer in a falling film, accounting for the first and second kind non-linear effects due to high concentration gradients resulting from chemical reaction in the liquid phase, takes the form (in dimensionless variables)

$$2(1+\bar{\rho}C)+\frac{\partial}{\partial Y}\left[(1+\bar{\mu}C)\frac{\partial U}{\partial Y}\right]=0,$$

$$\frac{\partial}{\partial X}[(1+\bar{\rho}C)U]+\frac{\partial}{\partial Y}[(1+\bar{\rho}C)V]=0, \tag{1}$$

$$Y=0,\quad U=V=0,$$

$$Y=H,\quad \frac{\partial U}{\partial Y}=0,$$

$$U\frac{\partial C}{\partial X}+V\frac{\partial C}{\partial Y}=Fo\frac{\partial}{\partial Y}\left[(1+\bar{D}C)\frac{\partial C}{\partial Y}\right]$$

$$-Da\,C+C\left(\frac{\partial U}{\partial X}+\frac{\partial V}{\partial Y}\right),$$

$$X=0,\quad C=0,$$

$$Y=H,\quad C=1,$$

$$Y=0,\quad \frac{\partial C}{\partial Y}=0, \tag{2}$$

$$A(1+\bar{D}C)\left(\frac{\partial C}{\partial Y}\right)_{Y=H}=H'U^*-V^*,$$

$$X=0,\quad H=1. \tag{3}$$

The relations between the dimensionless variables and parameters in equations (1)–(3) have the form

$$X=\frac{x}{l},\quad Y=\frac{y}{h_0},\quad U=\frac{u}{\bar{u}_0},\quad V=\frac{v}{\varepsilon\bar{u}_0},$$

$$C=\frac{c}{c^*},\quad H=\frac{h}{h_0},\quad \varepsilon=\frac{h_0}{l},\quad \bar{u}_0=\frac{gh_0^2\rho_0}{2\mu_0},$$

$$Fo=\frac{D_0 l}{\bar{u}_0 h_0^2},\quad Da=\frac{kl}{\bar{u}_0},\quad A=\bar{\rho}\,Fo,\quad \bar{\rho}=\frac{\rho^*-\rho_0}{\rho_0}. \tag{4}$$

In equations (1)–(3), it was accepted that the density, viscosity and diffusivity depend linearly on concentration

$$\rho=\rho_0(1+\bar{\rho}C),$$

$$\mu=\mu_0(1+\bar{\mu}C),$$

$$D=D_0(1+\bar{D}C), \tag{5}$$

where $\bar{\rho}$, $\bar{\mu}$ and $\bar{D}$ are small parameters. To verify this hypothesis it should be recalled that these characteristics of the absorbent change slightly with the concentration of the gas absorbed.

3. VELOCITY AND CONCENTRATION DISTRIBUTIONS IN THE FALLING FILM

To determine the velocity and concentration profiles in the film one has to solve the coupled system of boundary-value problems, i.e. equations (1)–(3). The solution depends on the small parameters $\bar{\rho}$, $\bar{\mu}$ and $\bar{D}$; so it might be sought in the form of a series truncated after the first-order approximations

$$\begin{aligned}U&=U_0+\bar{\rho}U_1+\bar{\mu}U_2+\bar{D}U_3,\\V&=V_0+\bar{\rho}V_1+\bar{\mu}V_2+\bar{D}V_3,\\C&=C_0+\bar{\rho}C_1+\bar{\mu}C_2+\bar{D}C_3,\\H&=H_0+\bar{\rho}H_1+\bar{\mu}H_2+\bar{D}H_3.\end{aligned} \tag{6}$$

Introducing equation (6) in equations (1)–(3) allows one to formulate the separate boundary-value problems from equation (6). Thus, considering the zero-order approximation, one obtains the problems accounting for the first kind non-linear effects only. Their solution was presented in ref. [3] and is of the form

$$\begin{aligned}U_0&=2H_0Y-Y^2,\\V_0&=-H_0'Y^2,\end{aligned} \tag{7}$$

$$C_0=\exp a_0\eta, \tag{8}$$

$$H_0=\left(1-\frac{3\varepsilon_0 a_0\xi}{2}\right)^{1/3}, \tag{9}$$

where

$$\varepsilon_0=\frac{\bar{\rho}\sqrt{(kD_0)}}{\varepsilon\bar{u}_0},\quad a_0=a-\sqrt{(a^2+1)}=-\sqrt{\left(\frac{\rho_0}{\rho^*}\right)},$$

$$a=\theta_0H_0^2H_0'=\frac{\rho^*-\rho_0}{2\sqrt{(\rho^*\rho_0)}},\quad \theta_0=\frac{\varepsilon\bar{u}_0}{\sqrt{(kD_0)}}. \tag{10}$$

Equations (8) and (9) were derived having in mind the fact that in the presence of a fast chemical reaction in the liquid the changes in concentration of the absorbed substance take place in a layer which is much thinner than the film. Because of this, a new coordinate system is introduced

$$\xi=X,\quad \eta=\frac{H_0-Y}{\theta},\quad \theta=\frac{\delta}{h_0},\quad \delta=\sqrt{\left(\frac{D_0}{k}\right)}, \tag{11}$$

where δ is an estimate for the thickness of the diffusive boundary layer in the presence of a first-order chemical reaction in a liquid film. The theoretical analysis indicates that the first kind non-linear effects are considerable when $\varepsilon_0>10^{-2}$, which is true if $k>10^4\ \mathrm{s}^{-1}$ or $\theta<10^{-2}$. That is why equations (8) and (9) were derived as a zero-order approximation in respect to the small parameter θ, and this restriction will be valid for all results that follow.

The second kind non-linear effects could be obtained as first-order approximations in respect to the small parameters in equation (6). The correction in the velocity distributions, accounting for the dependency of the density on concentration, could be found after the solution of the following boundary-value problem

$$\frac{\partial^2 U_1}{\partial Y^2}+2C_0=0,$$

$$\frac{\partial U_1}{\partial X}+\frac{\partial V_1}{\partial Y}+U_0\frac{\partial C_0}{\partial X}+V_0\frac{\partial C_0}{\partial Y}=0,$$

$$Y=0,\quad U_1=V_1=0,$$

$$Y=H_0,\quad \frac{\partial U_1}{\partial Y}=0. \tag{12}$$

The solution to equations (12) is straightforward

$$U_1=-2\left(\frac{\theta}{a_0}\right)^2\left\{\exp\left(\frac{a_0H_0}{\theta}\right)\times\left[\exp\left(-\frac{a_0Y}{\theta}\right)-1\right]+\frac{a_0Y}{\theta}\right\}. \tag{13}$$

Equation (13) indicates that U_1 is of the order of θ, while from the continuity equation (12) it follows that the same conclusion is valid for V_1; thus for the zero-order approximation in θ these corrections are zero.

In a similar manner one obtains the correction accounting for the dependence of viscosity on concentration

$$U_2=2\left(\frac{\theta}{a_0}\right)^2\exp\left(\frac{a_0H_0}{\theta}\right)\left[\exp\left(\frac{-a_0Y}{\theta}\right)\times\left(a_0\frac{H_0-Y}{\theta}-1\right)-\frac{a_0H_0}{\theta}+1\right]. \tag{14}$$

In this case the corrections U_2 and V_2 are again of the order of θ and, consequently, are also zero.

Similarly we obtain

$$U_3\equiv 0,\quad V_3\equiv 0,\quad C_i\equiv 0\quad (i=1,2),$$

$$C_3=\frac{2a_0^2}{4aa_0+3}(\exp a_0\eta-\exp 2a_0\eta). \tag{15}$$

The boundary-value problems for H_1 and H_2 are analogous

$$V_i^*-U_i^*H_0'-U_0^*H_i'=0,$$

$$\xi=0,\quad H_i=0,\quad i=1,2. \tag{16}$$

The solution to equations (16) has the form

$$H_i=\int_0^\xi \frac{V_i^*-U_i^*H_0'}{U_0^*}\,d\xi,\quad i=1,2. \tag{17}$$

Again, in equations (17) H_1 and H_2 are of the order of θ and consequently they are zero.

The boundary-value problem for H_3 is

$$\varepsilon_0\left(C_0\frac{\partial C_0}{\partial\eta}+\frac{\partial C_3}{\partial\eta}\right)_{\eta=0}=-U_0^*H_3',$$

$$\xi=0,\quad H_3=0. \tag{18}$$

The solution to equations (18) has the form

$$H_3=\frac{2\rho^*}{\rho^*+2\rho_0}(H_0-1). \tag{19}$$

A characteristic dimensional parameter h_0—the initial film thickness at $x=0$—is present in all results up to this place. It expresses the thickness of a liquid film, the flow regime of which is not influenced by the initial velocity profile ($\varepsilon=0$) and by the presence of non-linear effects ($x=0$). From this point of view, physically h_0 coincides with the thickness of an asymptotic film flow determined by Nusselt

$$h_0=\left(\frac{3\mu_0Q_0}{\rho_0 g}\right)^{1/3}. \tag{20}$$

4. INFLUENCE OF THE NON-LINEAR EFFECTS ON THE MASS TRANSFER KINETICS

The mass transfer rate could be expressed by means of the film-length averaged flux of substance through the interface

$$J=\beta Mc^*=-\frac{1}{l}\int_0^l I\,dx. \tag{21}$$

The flux I was found in ref. [3] to be

$$I=\frac{MD_0\rho^*}{\rho_0\sqrt{(1+h'^2)}}\left[\left(1+\bar{D}\frac{c}{c^*}\right)\left(h'\frac{\partial c}{\partial x}-\frac{\partial c}{\partial y}\right)\right]_{y=h}, \tag{22}$$

which allows the determination of the mass transfer coefficient

$$\beta=\frac{\rho^*D_0}{lc^*\rho_0}\int_0^l\left[\left(1+\bar{D}\frac{c}{c^*}\right)\times\frac{\partial c/\partial y)-h'(\partial c/\partial x)}{\sqrt{(1+h'^2)}}\right]_{y=h}dx. \tag{23}$$

Introducing the variables from equations (11) yields

$$\beta=-\sqrt{(kD_0)}\frac{\rho^*}{\rho_0}\int_0^1\left[(1+\bar{D}C)\frac{\partial C}{\partial\eta}\right]_{\eta=0}d\xi, \tag{24}$$

or, with accuracy to the first-order approximation in $\bar{D}$, it follows that

$$\beta=\sqrt{(kD_0)}\sqrt{\left(\frac{\rho^*}{\rho_0}\right)}\left(1+\bar{D}\frac{\rho^*}{\rho^*+2\rho_0}\right). \tag{25}$$

The mass transfer coefficient in a falling film in the presence of absorption and chemical reaction, neglecting the non-linear effects [4], has the form

$$\beta_0=\sqrt{(kD_0)}. \tag{26}$$

Comparison of equations (25) and (26) yields an explicit expression for the non-linear effects

$$\frac{\beta}{\beta_0}=\sqrt{\left(\frac{\rho^*}{\rho_0}\right)}\left(1+\bar{D}\frac{\rho^*}{\rho^*+2\rho_0}\right). \tag{27}$$

An increase of the chemical reaction rate results in the decrease of the parameter θ_0, and when $k>10^8\,s^{-1}$ the hydrodynamics does not influence the mass transfer any more because $\theta_0 < 10^{-2}$ and the problem can be solved in zero-order approximation in θ_0. The new solutions are straightforward as far as from equations (10) it follows that when $\theta_0 = 0$, $a = 0$ and $a_0 = -1$. Thus, equations (8), (9), (15) and (19) take the form

$$C_0 = \exp(-\eta),$$
$$C_3 = \tfrac{2}{3}[\exp(-\eta) - \exp(-2\eta)],$$
$$H_0 = \left(1 + \frac{3\varepsilon_0 \xi}{2}\right)^{1/3},$$
$$H_3 = \tfrac{2}{3}(H_0 - 1), \tag{28}$$

while for the mass transfer coefficients one could write

$$\beta = \sqrt{(kD_0)}\,\frac{\rho^*}{\rho_0}\left(1 + \frac{\bar{D}}{3}\right), \tag{29}$$

or, in the explicit form, the expression for the non-linear effects is

$$\frac{\beta}{\beta_0} = \frac{\rho^*}{\rho_0}\left(1 + \frac{\bar{D}}{3}\right). \tag{30}$$

5. CONCLUSIONS

The theoretical analysis of the influence of some non-linear effects on the mass transfer kinetics in falling films implies the following more important conclusions:

(a) there exists a limiting chemical reaction rate ($k > 10^4$ s^{-1}), when the first kind non-linear effects are considerable;
(b) when $k > 10^8$ s^{-1} the influence of hydrodynamics on convective diffusion is negligible;
(c) the second kind non-linear effects, connected with the dependence of the diffusivity on concentration, influence the diffusion process only, while the hydrodynamics is practically independent of them;
(d) the second kind non-linear effects, connected with the dependency on concentration and with the viscosity practically do not influence the hydrodynamics and the diffusion processes in falling films.

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INFLUENCE DE QUELQUES EFFETS NON-LINEAIRES SUR LA CINETIQUE DU TRANSFERT DE MASSE DANS DES FILMS LIQUIDES TOMBANTS

Résumé—Une théorie non-linéaire du phénomène de transfert de masse dans les films tombants est présentée dans le cas d'absorption de gaz et d'une réaction chimique rapide dans le film. Une analyse de perturbation est développée pour étudier l'influence des gradients de concentration élevés et dûs à une très fine couche limite de diffusion dans le film avec réaction chimique. L'existence d'effets non-linéaires de seconde espèce, résultants des grands gradients de concentration, a été montrée et on a estimé quantitativement leur influence sur le flux de transfert massique.

DER EINFLUSS EINIGER NICHTLINEARER EFFEKTE AUF DIE KINETIK DES STOFFÜBERGANGS IN FALLENDEN FLÜSSIGKEITSFILMEN

Zusammenfassung—Es wird eine nichtlineare Theorie der Stoffübergangsphänomene in fallenden Flüssigkeitsfilmen mit Gasabsorption und schnellen chemischen Reaktionen im Film dargestellt. Die Betrachtung wurde mit der Störungstheorie durchgeführt, um den Einfluß großer Konzentrationsgradienten auf sehr dünne Diffusionsgrenzschichten im Film mit chemischer Reaktion zu untersuchen. Die Existenz nichtlinearer Effekte zweiter Art aufgrund der großen Konzentrationsgradienten wurde nachgewiesen und quantitative Abschätzungen dieser Einflüsse auf den Stoffübergang abgeleitet.

ВЛИЯНИЕ НЕКОТОРЫХ НЕЛИНЕЙНЫХ ЭФФЕКТОВ НА КИНЕТИКУ МАССОПЕРЕНОСА В СТЕКАЮЩИХ ПЛЕНКАХ

Аннотация—Предложена нелинейная теория массопереноса в стекающих пленках при абсорбции газа и протекании быстрой химической реакции. С использованием метода возмущений исследована роль больших градиентов концентрации в весьма тонком диффузионном пограничном слое в пленке с химической реакцией. Показано существование нелинейных эффектов второго рода из-за больших градиентов концентрации и даны количественные оценки их влияния на скорость массопереноса.