Effect of Interfacial Turbulence on the Rate of Absorption

ELI RUCKENSTEIN

Clarkson College of Technology, Potsdam, New York

In a recent significant contribution, Brian, Vivian, and Matiatos (*1*) have drawn attention to the severe disagreement existing between the penetration theory and data available in the literature for the absorption of carbon dioxide into monoethanolamine. Performing experiments on the absorption of carbon dioxide with simultaneous desorption of inert tracer propylene in a short, wetted wall column, they reached the conclusion that the discrepancies are due to interfacial turbulence driven by surface tension gradients. The desorption of propylene without absorption of carbon dioxide agrees closely with the predictions of the penetration theory. If, however, both processes take place simultaneously, the rate of desorption is greatly increased. This enhancement must be linked to a hydrodynamic effect induced by the absorption of carbon dioxide, and Brian, Vivian, and Matiatos conclude that the only hydrodynamic process which can occur in the above mentioned situation is due to the interfacial turbulence generated by the Marangoni effect. No interfacial activity was observed, but this was explained by the small scale and small intensity of the induced turbulence.

In what follows, results obtained by means of a roll-cell model proposed by the author (*2*) for describing interfacial turbulence will be used for a qualitative discussion of the mentioned experiments. On the basis of the model, it was possible to show that a small scale turbulence of small intensity, due to Marangoni instability, leads to a large increase of the rate of mass transfer, of the same order of magnitude as the ones reported by Brian et al. There are some other experiments (*3* to *6*) in which the effect of interfacial turbulence was important. Our evaluations are compatible with those data too.

THE MODEL

By means of the linearized instability theory, it was shown that interfacial turbulence is a consequence of hydrodynamic instability induced by the Marangoni effect (*7*) and that a chemical reaction may have an important effect on the occurrence of interfacial turbulence (*8*). As in the analogous case of bulk turbulence, the linearized instability theory is able to explain the occurrence of turbulence, but it gives no information about the velocity distribution of the stable (unsteady turbulent) state and hence about the corresponding rate of mass transfer. Because the hydrodynamic problem has not yet been solved, it is not possible at the present stage to predict the rate of mass transfer in turbulent condition (either bulk or interfacial turbulence) from first principles. The theoretical tools used for bulk turbulence are based largely either on the turbulent diffusion concept, or on a physical model. Such a type of analysis of the effect of interfacial turbulence on mass transfer was made (*2*) by using a model in which one considers that near the interface the elements of liquid have a translatory motion with the average local velocity upon which circulatory motions in roll cells propagating with the average velocity are superposed. Arguments in support of this model were adduced in our previous paper (*2*) and in some recent experiments (*9*) in which the turbulent fluctuations are simulated by pulses.

It is possible to use simple analytical expressions for the velocity components compatible with the above model. Such expressions are, for instance

$$u = u_0 \{1 + A [\sin k (x - wt)] [\cos k_1 y]\} \tag{1}$$

$$v = -\frac{Aku_0}{k_1} [\cos k(x - wt)] [\sin k_1 y] \tag{2}$$

The first term in the expression of u represents the translatory velocity and the second the superposed roll-cell motion. Since the roll cells are considered as propagating with the average liquid velocity u_0, the wave velocity w is equal to u_0. Interfacial turbulence is due to an instability occurring because of the interaction between the velocity and the concentration fields. The parameters A, k, and k_1 must depend on the concentration and the concentration gradient, and consequently on x. It is also expected that the interfacial turbulence will decay with the distance to the interface. For reasons of simplicity, however, it will be considered that the above parameters are quasi-constants.

In the case of pure absorption, the following equation has been obtained, on the basis of the model presented above, for the rate of absorption in a thin liquid film flowing along a vertical wall (*10*):

$$\overline{N}_1 = \left(\sqrt{\frac{Du_0}{\pi x}}\right) (c_i - c_0)\, \overline{\psi} \tag{3}$$

where $\overline{N}_1$ is the time average of the mass flux at the free interface, and

$$\overline{\psi} = \begin{cases} 1 \text{ for } x \rightarrow 0 \\ \overline{\psi}(\alpha_0) \text{ for sufficiently large values of } x \end{cases} \tag{4}$$

Some values of the function $\overline{\psi}(\alpha_0)$ are given in Table 1; α_0 is a dimensionless group defined by

$$\alpha_0 \equiv \frac{Aku_0}{Dk_1^2} \tag{5}$$

When diffusion is accompanied by a first-order chemical reaction and $c_0 = 0$, the time average mass flux at the free interface is given by

$$\overline{N} = \frac{k_r}{u_0} \int_0^x \overline{N}_1\, e^{-\frac{k_r}{u_0}x} dx + \overline{N}_1\, e^{-\frac{k_r}{u_0}x} \tag{6}$$

where $\overline{N}_1$ represents the time average diffusion flux at the interface for the convective diffusion case. This quantity is given by Equation (3). Values for $\overline{\psi}$ are available only for two limiting conditions [see Equation (4)]. Consequently, one may obtain from (6) expressions for $\overline{N}$ valid also for some limiting conditions. For small values of the reaction rate constant, it results from Equation (6) that the amplification of the mass flux at the interface produced by the existence of the roll cells (compared with the situation without roll cells corresponding to the penetration theory) is equal to $\overline{\psi}$. For large values of only k_r, the values of $\overline{N}_1$ corresponding to small values of x contribute appreciably to the value of the integral; because for small values of x we have $\overline{\psi} = 1$, it results that no amplification exists. Consequently, the amplification factor defined as the ratio between the mass flux when the roll cells are present and when they are not has for a chemical reaction of the first order an upper bound given by $\overline{\psi}$ (α_0). The amplification factor in the case in which a case without chemical reaction. The comparison is made for the same values of α_0.

DISCUSSION

The new main physical quantity which appears in all the above situations is the dimensionless quantity α_0. It may be considered as the product of a Peclet number u_0/Dk_1 and a cell number Ak/k_1. The group α_0 contains, however, the unknown quantities A, k, and k_1 for which the above model gives no information. Evaluations of these quantities will be made on the basis of some very simplified considerations.

The velocity at the interface is replaced by its average value $U = u_0\left(1 \pm \frac{2A}{\pi}\right)$ over the dimension $x_0 = \pi/k$ of the cell. Thus one may consider that, in the average, over the distance x_0, the Marangoni effect is acting as if a plate having the velocity U is moving along the interface.

The velocity distribution near the interface is approximated by that valid near a plate which is moving with the velocity U into a liquid having the velocity u_0 at a sufficiently long distance from the interface (the velocity at the interface without the Marangoni effect). Because x_0 is very short, the corresponding thickness of the hydrodynamic boundary layer is also very small, and that distance (though small) may be taken as infinitely large in the calculations. Owing to the Marangoni effect, the shear stress at the free interface is given by

$$\tau = -\frac{d\sigma}{dx}$$

and the average shear stress over the dimension x_0 of a cell by

$$\overline{\tau}\, x_0 \equiv \int_0^{x_0} \tau dx = -\Delta\sigma \qquad (7)$$

Calculating the shear stress τ by using the velocity distribution valid near a plate moving into a semi-infinite liquid, as given in reference *11*, Equation (7) becomes

$$2\,\rho\nu^{1/2}\,u_0^{3/2}\left(1+\frac{2\,|A|}{\pi}\right)^{3/2}\frac{A}{\pi}\left(\frac{\pi}{k}\right)^{1/2} = |\Delta\sigma| \qquad (8)$$

Because $|A| << 1$, Equation (8) may be written as

$$2\,\rho\nu^{1/2}\,u_0^{3/2}\,\frac{A}{\pi}\left(\frac{\pi}{k}\right)^{1/2} = |\Delta\sigma| \qquad (9)$$

The instability theory may give some information about the dimensions of the roll cells if one assumes that they are of the order of magnitude of the dominant wave length (the wave length for which the growth of the perturbation is maximum). Instability results are, however, available only for nonflow conditions (*7, 8*), and very small modifications of the coupled hydrodynamic and convective-diffusion equations introduce big differences even in the conditions of occurrence of the instability (*8*). Moreover, the calculated dominant wave lengths are about one order of magnitude smaller than the dimensions of the cells observed (*12*). Because the values observed experimentally are of the order of 10^{-1}-10^{-2} cm. (*12*), the evaluations will be made for the lower limit $x_0 \approx 10^{-2}$ cm. For evaluating the values of α_0 and A, let us consider $\Delta\sigma = 10^{-3}$ dynes/cm., $\nu = 10^{-2}$ sq.cm./sec., $\rho = 1$ g./cc., $D = 2.10^{-5}$ sq.cm./sec., $u_0 = 100$ cm./sec., $k = k_1$, and $x_0 = 10^{-2}$ cm. One obtains $\alpha_0 = 2.5$ and $A = 1.57 \times 10^{-4}$. If $\Delta\sigma$ is taken as 10^{-2} dynes/cm. while the other quantities remain the same, one gets $\alpha_0 = 25$ and $A = 10^{-3}$. The amplifications are large, in both cases being 3.25 for $\alpha_0 = 2.5$ and > 6 for $\alpha_0 = 25$. Brian et al. have obtained for the rate of desorption of propylene when it is accompanied by simultaneous carbon dioxide absorption, values which are an order of magnitude larger than those obtained without simultaneous absorption. The rate of absorption of carbon dioxide (in this case diffusion is accompanied by a chemical reaction) is also much larger than predicted by the penetration theory, but the amplification factor is smaller than for pure mass transfer. One may stress the fact that such a difference between the values of the amplification factor for the cases without and with a chemical reaction was predicted above [see the comment after Equation (6)]. The evaluated amplifications of the mass flux are large, of the same order of magnitude as the ones obtained experimentally, though for $A = 10^{-3}$ the convective motion due to the roll cells induced by the Marangoni effect is very slow. It is natural not to observe visually motions having a scale of 10^{-2} cm. and an intensity of 10^{-3}. What is significant and must be stressed is the fact that very small values of $\Delta\sigma$ may lead to large amplifications.

The above evaluations are compatible with the amplifications equal about to two observed by Backer et al. (*5*) who have investigated the transfer of acetic acid or acetone between water and carbon tetrachloride or with the amplifications up to 10 obtained by Clark and King (*6*) for a similar physical situation.

NOTATION

A = ratio between the amplitude of oscillation of the velocity u and u_0
c = concentration
c_i = concentration at the interface
c_0 = value of c for $x = 0$
D = molecular diffusion coefficient
k = wave number along the x direction
k_1 = wave number along the y direction
k_r = reaction rate constant
N = mass flux

TABLE 1

α_0	0	1	1.5	2	2.5	3	3.5	4
$\overline{\psi}\,(\alpha_0)$	1	1.20	1.52	2.10	3.25	4.45	5.35	5.95

N_1 = mass flux in the case without chemical reaction
$\overline{N}, \overline{N}_1$ = temporal averages of N and N_1
t = time
u = x velocity component
u_0 = average velocity
v = y velocity component
w = propagation velocity of the roll-cells
U = average velocity at the interface with respect to x over a cell
x = distance along the interface
x_0 = length of a cell along the x direction
y = distance from the interface
z = $k(x - wt)$

Greek Letters

α_0 = quantity defined by Equation (5)
$\overline{\psi}$ = average with respect to time of the ratio between the mass flux when roll cells are acting and the mass flux resulting from the penetration theory
μ = dynamic viscosity
ν = kinematic viscosity
ρ = density
σ = surface tension
$\Delta\sigma$ = difference between the values of σ at the end and at the beginning of each cell
τ = shear stress at the interface
$\overline{\tau}$ = average of τ with respect to x

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The Periodic Viscous Sublayer Model and Heat Transfer to Drag Reducing Solutions

R. L. MEEK and A. D. BAER

Bell Telephone Laboratories, Inc., Murray Hill, New Jersey

In a recent paper (*11*), the Einstein-Li (*7*) concept of a periodic viscous sublayer at the bounding surfaces of a turbulent shear flow was reintroduced, and supporting experimental evidence was presented. The essential characteristics of the Einstein-Li model, which is a limiting case of a more rigorous model recently developed by Black (*1, 2*), are that, at a point on the wall, turbulent fluctuations suddenly penetrate to very near the surface, that these penetrations occur with a fairly well-defined regularity, and that between penetrations viscous processes dominate the sublayer flow. The virtue of such a treatment is that it allows prediction of heat and mass transfer to turbulently flowing fluids from the constitutive and state equations and physical properties (including any generation or rate constants), since only the well-known differential equations describing molecular transport need be solved. At the present stage of development of the model, the fluctuation period is obtained from friction factor data. Reference *10* may be consulted for a complete discussion and development of the model as well as critical evaluation of the assumptions involved.

THE SUBLAYER MODEL

Extensive data have been presented elsewhere (*10, 11*) in support of the periodic viscous sublayer model. The variable of principal interest is the mean period between turbulent penetrations T or, in dimensionless form, T^+, where $T^+ \equiv \sqrt{T/\nu}\, u_*$. (The fluid kinematic viscosity is designated ν and u_* is the friction velocity.) The result of the sublayer model calculation (*10, 11*) is that for Reynolds numbers N_{Re} greater than 10^4, the dimensionless mean period is essentially constant at 18. We may note immediately from this that the mean frequency of penetrations is proportional to u_*^2/ν.

It is of interest to compare this model prediction with the recent visual observations of Corino and Brodkey (*4*). Table 1 reproduces the data of Figure 8 of that paper, where average number of disturbances per second at a point on the wall have been converted to dimensionless mean periods. The agreement with the calculated value of $T^+ = 18$ is quite satisfactory.

TURBULENT FLOW OF AND HEAT TRANSFER TO DRAG REDUCING SOLUTIONS

Heat transfer to dilute polymer solutions which exhibit the Toms effect (*17*) has of late attracted a great deal of

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A. D. Baer is at the University of Utah, Salt Lake City, Utah.