Int. J. Heat Mass Transfer. Vol. 26, No. 7, pp. 981-991, 1983
Printed in Great Britain

0017-9310/83 \$3.00 + 0.00
Pergamon Press Ltd.

MASS TRANSFER INTO A TURBULENT LIQUID FILM

A. K. Biń
Institute of Chemical Engineering, Warsaw Technical University, ul. Waryńskiego 1, 00-645 Warszawa, Poland

(*Received* 27 *August* 1982)

Abstract—Different authors' attempts to apply the eddy diffusivity model to the description of mass transfer into a turbulent falling liquid film have been reviewed and compared. The main emphasis has been put on the range of the model applicability and its links with the basic physical and hydrodynamic properties of the studied systems. It has been shown that surface tension does not affect mass transfer coefficients.

NOMENCLATURE

a,	eddy diffusivity parameter $[\mathrm{m}^{2-n}\ \mathrm{s}^{-1}]$;
C_{ij},	numerical constant in the ith equation;
c,	concentration of the solute $[\mathrm{kmol\ m^{-3}}]$;
c_0,	inlet concentration $[\mathrm{kmol\ m^{-3}}]$;
c_s,	interfacial concentration $[\mathrm{kmol\ m^{-3}}]$;
d,	tube diameter [m];
D,	molecular diffusivity $[\mathrm{m^2\ s^{-1}}]$;
D_t,	eddy diffusivity $[\mathrm{m^2\ s^{-1}}]$;
g,	gravitational acceleration $[\mathrm{m\ s^{-2}}]$;
k_L,	local mass transfer coefficient $[\mathrm{m\ s^{-1}}]$;
$\bar{k}_L$,	average mass transfer coefficient $[\mathrm{m\ s^{-1}}]$;
l_L,	integral macroscale of eddies [m];
l_m,	Taylor microscale of eddies [m];
L,	column or plate length [m];
n,	power exponent in equation (1);
Re_L,	film Reynolds number, $4\bar{u}\delta/\nu$;
Sc,	Schmidt number, ν/D;
Sh,	local film Sherwood number, $k_L\delta/D$;
Sh_m,	mean film Sherwood number, $\bar{k}_L\delta/D$;
$\bar{u}$,	average film velocity $[\mathrm{m\ s^{-1}}]$;
u_s,	surface film velocity $[\mathrm{m\ s^{-1}}]$;
v_0,	characteristic turbulence velocity $[\mathrm{m\ s^{-1}}]$;
v^*,	friction velocity $[\mathrm{m\ s^{-1}}]$;
$\bar{v}_x$,	mean local velocity in x direction $[\mathrm{m\ s^{-1}}]$;
$\bar{v}'_x$,	fluctuation velocity in x direction $[\mathrm{m\ s^{-1}}]$;
x,	axial coordinate [m];
X,	dimensionless axial distance, $a^{2/n}x/(D^{2/n-1}u_s)$;
y,	transverse coordinate measured from the interface [m].

Greek symbols

β,	dimensionless eddy diffusivity group, $a^{2/n}\delta^2/D^{2/n}$;
δ,	film thickness [m];
ε,	energy dissipation rate per unit liquid mass $[\mathrm{m^2\ s^{-3}}]$;
$\bar{\varepsilon}$,	average energy dissipation rate per unit liquid mass $[\mathrm{m^2\ s^{-3}}]$;
θ,	dimensionless concentration, $(c_s-c)/(c_s-c_0)$;
λ,	thickness of zone of damped turbulence [m];
ν,	kinematic viscosity $[\mathrm{m^2\ s^{-1}}]$;
ρ,	liquid density $[\mathrm{kg\ m^{-3}}]$;
σ,	surface tension $[\mathrm{N\ m^{-1}}]$;
ϑ_z,	characteristic linear dimension, $(\nu^2/g)^{1/3}$ [m];
Ψ,	dimensionless group, $Sh(\pi X/\beta)^{1/2}$;
Ψ_m,	dimensionless group, $Sh_m(\pi X/\beta)^{1/2}$.

INTRODUCTION

THE PROBLEM of liquid-phase-controlled mass transfer into a turbulent liquid film has been studied experimentally and theoretically by many authors. In the majority of theoretical attempts the concept of eddy diffusivity has been used. This had firstly been introduced for film flows by Levich [1] and was later discussed and/or modified by other authors [2–7]. According to these authors the eddy diffusivity can be approximated as

$$D_t = ay^n \tag{1}$$

where y is the distance normal to the interface. This approximation is probably valid only very close to the interface (i.e. throughout the zone of primary resistance which is much smaller than the thickness of the zone where eddies are damped in typical gas–liquid systems with low liquid-phase molecular diffusivity).

Some authors tried to apply an eddy cell model to mass transfer into a turbulent film flow [8–10]. These authors had to make numerous assumptions concerning characteristic turbulence scales and wave parameters in order to estimate mass transfer coefficients from their eddy cell models. As pointed out by Henstock and Hanratty [7] the eddy cell models seem to be equivalent to the eddy diffusivity model. However, their application to the film flow is not completely convincing because of the questionable assumptions made and uncertainties in the wave and turbulence characteristics. Therefore, the model based on the eddy diffusivity concept is preferred in the following considerations. It has also been successfully applied to the case of absorption with chemical reaction in a turbulent film flow [11–15].

On the other hand, as pointed out by Gottifredi and Quiroga [15], the eddy diffusivity model is equivalent to the surface renewal model when convective transport parallel to the interface is neglected. This equivalence is not formal but has been established on the basis of an analytical solution derived by these authors. Since D_t is directly related to the hydrodynamic parameters of the system [2] through the parameter a in equation (1), the eddy diffusivity model seems to be more convenient for interpretation.

The main objective of this work is to discuss the eddy diffusivity model with the main emphasis put on the range of its agreement with the hitherto published experimental data on mass transfer into a turbulent film flow.

EDDY DIFFUSIVITY MODEL

The mass balance for the absorbed component in 2-dim., fully-developed film flow may be written in terms of an eddy diffusivity as

$$u(y)\frac{\partial \theta}{\partial x} = \frac{\partial}{\partial y}\left[(D+ay^n)\frac{\partial \theta}{\partial y}\right] \qquad (2)$$

where $u(y)$ is the velocity component in the x direction, θ is the dimensionless concentration and D is the molecular diffusivity. Equation (2) neglects axial transport and assumes no diffusion-induced velocity. a and n are assumed to be independent of x (or time). The boundary conditions of interest are as follows:

$$\begin{aligned} x &= 0, & \theta &= 1, \\ y &= 0, & \theta &= 0, \\ y &= \delta, & \frac{\partial \theta}{\partial y} &= 0. \end{aligned} \qquad (3)$$

The first condition expresses the fact that the liquid enters the mass transfer section completely mixed. The second condition states that the concentration remains constant at the gas–liquid interface and the third one that no transfer occurs across the solid boundary.

Usually two simplifying assumptions are made in solving equation (2) with boundary conditions given by equations (3). Firstly, $u(y)$ is replaced by u_s, its surface value which can be taken as a constant for the case of no shear at the interface, and when the penetration depth of the absorbed component is small in comparison with the corresponding thickness where u changes significantly. It is also assumed that the eddy diffusivity given by equation (1) for the interfacial region is valid over the complete film thickness. This assumption should not lead to any significant error since the major resistance to mass transfer is concentrated close to the interface for systems with large Schmidt numbers.

Solutions of equation (2) with boundary conditions given by equations (3) were first discussed by King [2]. He obtained two asymptotic solutions for the case of very short contact times and for very long contact times. For very short contact times, the eddy diffusivity term has no effect on the rate of mass transfer and equation (2) yields the classical penetration solution

$$\Psi = Sh(\pi X/\beta)^{1/2} = 1. \qquad (4)$$

For long contact times (long films) the concentration profiles become fully-developed and the steady-state diffusion takes place. Thus equation (2) simplifies, with the LHS equal to zero, to give the following solution [2, 4, 7]:

$$k_L = \frac{n}{\pi}\sin(\pi/n)a^{1/n}D^{1-1/n} \qquad (5)$$

or

$$\Psi = \frac{n}{\sqrt{\pi}}\sin(\pi/n)X^{1/2}. \qquad (6)$$

Most of the experimental data for mass transfer into turbulent film flow indicate that the exponent n is close to 2 [3–11, 22, 27, 30, 32]. This evidence allowed equation (2) to be solved for $n = 2$. Several results of the complete solution of this equation are available in the references. Sandall [16] presented an empirical equation based on the results of numerical computations which can be expressed as

$$\Psi = 1+0.3500X \qquad (7)$$

valid for $X \leqslant 2.5$.

Subramanian [17] introduced a method of solution of equation (2) valid for short contact times which allowed the results to be obtained in a simpler and more accurate way compared with Sandall's approximation. Kishinevskiy and Korniyenko [18], based on Sandall's data, proposed an equation for the average mass transfer coefficient which can be differentiated to give the local values of k_L and correspondingly

$$\Psi = \frac{2}{\sqrt{\pi}}X^{1/2}[\coth(0.5641X^{1/2}) - 0.2820X^{1/2}\sinh^{-2}(0.5641X^{1/2})]. \qquad (8)$$

Equation (8) can be applied for all values of $X > 0$.

Yih and Seagrave [14] presented an analytical method of solution of equation (2) based on the series expansion with the eigenvalues and eigenfunctions. Gottifredi and Quiroga [13] obtained an approximated solution which covers the whole range of the parameter X,

$$\Psi = (\pi X)^{1/2}\left\{\frac{\exp(-4X/\pi^2)}{(\pi X)^{1/2}} + \frac{2}{\pi}\operatorname{erf}[4/(\pi^2 X)^{1/2}]\right\}. \qquad (9)$$

From the practical point of view the average values of the mass transfer coefficients are of interest since they can be directly compared with the experimental data. Integration over the film length gives the expressions for the mean Sherwood number based on the average mass transfer coefficients. The values of Ψ_m obtained are listed in Table 1.

As can be seen from the data shown in Table 1, the short contact times asymptote corresponds to the value of $\Psi_m = 2$, whereas the long contact times asymptote, equation (6) with $n = 2$, is practically attained at $X \gtrsim 20$. Also, the solution presented by Yih and Seagrave [14] seems to yield less accurate results for small values of X ($\leqslant 1$) and for large values of X ($\geqslant 50$), apparently because of the limited number of terms available for calculations.

Table 1. Values of Ψ_m for different authors' solutions

X	Sandall [16]	Subramanian† [17]	Kishinevskiy and Korniyenko [18]	Yih and Seagrave† [14]	Gottifredi and Quiroga [13]	Equation (6) with $n = 2$
0.01	2.00230	2.00333	2.00212		2.00270	
0.05	2.01167	2.01654	2.01060	1.5908	2.01348	
0.10	2.02334	2.03283	2.02118	1.7318	2.02691	
0.50	2.1167	2.15417	2.10499	2.0219	2.13244	
0.80	2.1867	2.23467	2.16695	2.1367	2.20951	
1.0	2.2334	2.28333	2.20784	2.1625	2.25998	
2.0	2.4668		2.40743	2.4588	2.5049	
5.0			2.96318	3.1195	3.1438	2.52313
10.0			3.77550	3.9864	4.0118	3.56825
20.0			5.11167	5.2926	5.3599	5.04627
50.0			7.98432	7.7752	8.1772	7.97885
100.0			11.28379	10.1423	11.4241	11.28379
200.0			15.95769		16.0569	15.95769
500.0			25.23132		25.2941	25.23132
1000.0			35.68248		35.7268	35.68248

† With two terms of the expression.

‡ The highest values obtained for different β.

EDDY DIFFUSION PARAMETER

The main problem which now emerges is the formulation of an expression for the parameter a in equation (1) describing the eddy diffusivity. The relationships suggested for a by different authors are listed in Table 2.†

An inspection of the expressions listed in Table 2 shows that: (i) not all of them take into account the effect of surface tension, (ii) some of them contain the characteristic turbulence velocity, v_0, frequently substituted by the friction velocity, v^*, which for the vertical film flow is taken as‡

$$v^* = (g\delta)^{1/2}. \tag{17}$$

Equation (12), after substitution into equation (5), yields an expression which shows that $k_L \propto \bar{\varepsilon}^{1/4}$, independent of n. Equation (16) has been derived by the authors under the assumption of a two-parametric model of mass transfer, incorporating two turbulence scales, i.e. v^* for the velocity scale and the film thickness, δ, for the length scale. Actually, equation (13) due to Prasher and Fricke [5] also includes two parameters, i.e. δ and $\bar{\varepsilon}$, although it has been derived from dimensional arguments. Equation (14) is the result of an attempt to link the Levich–Davies model with equation (5) for $n = 2$. The authors [18] estimated the value of the numerical constant to be about 15 by fitting their model equation to a small number of selected experimental data from different authors. Moreover, they also claimed that this constant has a universal character for all mass transfer processes at turbulent free surfaces. Equation (15) has been obtained from dimensional considerations based on the Prandtl mixing length and after fitting to the experimental data of different authors collected for sufficiently long films and the systems with large Schmidt numbers. (The necessary condition can be expressed as $Re_L^{\prime}Sc \to \infty$.)

For the further analysis of the problem it is necessary to consider basic film flow parameters such as:

the mean film thickness

$$\delta = C_{18}\vartheta_z Re_L^m, \tag{18}$$

the average velocity of the film

$$\bar{u} = \left(\frac{1}{4C_{18}}\right)(\nu g)^{1/3} Re_L^{1-m}, \tag{19}$$

Table 2. Relationships suggested for a in equation (1)

Authors	Relationship	Equation	Notes
Levich [1]	$a \propto v_0/\lambda = \rho v_0^3/\sigma$	(10)	$n = 2$
Davies [3]	$a \propto \rho v_0^3/\sigma_{eq}$	(11)	$n = 2$
King [2]	$a \propto (\bar{\varepsilon}^n/\nu^{3n-4})^{1/4}$	(12)	
Prasher and Fricke [5]	$a \propto (\rho/\sigma)(\delta^3\bar{\varepsilon}^3/g\nu)^{1/2}$	(13)	$n = 2$
Kishinevskiy and Korniyenko [18]	$a = C_{14}\rho v_0^3/\sigma_{eq}$	(14)	$n = 2$ $C_{14} = 15$
Carrubba [6]	$a = C_{15} Re_L^{2.50}\nu/\delta^2$	(15)	$n = 2$ $C_{15} = 6.09 \times 10^{-8}$
Henstock and Hanratty [7]	$a \propto v_0^3\delta/\nu^2$	(16)	$n = 2$

---

† Henstock and Hanratty [7] listed a similar table but they did not include some of the relationships given above.

‡ Henstock and Hanratty's theory introduces the coefficient 2/3 under the square root.

the surface velocity of the film

$$u_s = C_{20}\bar{u}, \tag{20}$$

the rate of energy dissipation for a vertically falling film

$$\bar{\varepsilon} = g\bar{u}. \tag{21}$$

Different values of the exponent m are quoted in the references by different authors: values range from 0.5 to 0.667 [19–25]. Most frequently, in discussions on mass transfer into turbulent falling films, expressions suggested by Brötz [19], Brauer [20] and Feind [21] are used. More recently, Takahama and Kato [25] gave the values of $C_{18} = 0.228$ and $m = 0.526$. A comparison of the calculations based on the constants given by Takahama and Kato and those suggested by earlier authors shows that the relationships of Brötz, Brauer, Feind, Zhivaykin and Volgin [23] and Ueda *et al.* [24] differ by less than 10% for the range of Re_L met in practice. Somewhat greater deviations (−14%) result for the average film thickness calculated from the complicated formula given by Henstock and Hanratty [7]. Further considerations are mainly based on the Takahama and Kato's values of C_{18} and m.

The surface velocity of the film is greater than the average film velocity by a factor of 1.3–1.5 [25, 26, 35].

Substitution of equation (18) into equation (17) yields

$$v^* = C_{18}^{1/2}(vg)^{1/3}\,Re_L^{m/2}. \tag{22}$$

Therefore, for the Levich–Davies models, $a \propto Re_L^{3m/2}$ and, if equation (5) with $n = 2$ is used (under the assumption of a sufficiently long film), then it can be concluded that $k_L \propto Re_L^{3m/4}$. Since King's model, equation (12), indicates that $a \propto \bar{\varepsilon}^{1/4}$, then, by taking into account equations (21) and (18), one can conclude that $a \propto Re_L^{(1-m)/2}$ and $k_L \propto Re_L^{(1-m)/4}$.

In the case of equation (13), after substitution of equations (18), (21) and (19) for the film thickness and the energy dissipation, the following equation can be obtained:

$$a = C_{23}\left(\frac{1}{4}\right)^{3/2}\left(\frac{\rho g v}{\sigma}\right) Re_L^{3/2}. \tag{23}$$

The form of equation (23) indicates that with $n = 2$, $k_L \propto Re_L^{3/4}$, independent of m. Substitution of equation (18) into equation (15) leads to the following expression:

$$a = (C_{15}/C_{18}^2)(g^2/v)^{1/3}\,Re_L^{2.50-2m} \tag{24}$$

whereas in the case of equation (16) one can obtain

$$a = C_{25}C_{18}^{5/2}(g^2/v)^{1/3}\,Re_L^{5m/2}. \tag{25}$$

It follows from equation (24) that $k_L \propto Re_L^{1.25-m}$ and from equation (25) that $k_L \propto Re_L^{5m/4}$.

Kishinevskiy and Korniyenko [18] used for v_0 an expression given by Brötz [19]

$$v_0 = C_{26}\bar{u} \quad \text{with } C_{26} = 0.0712 \tag{26}$$

which leads to the following relationship:

$$a = C_{14}[C_{26}/(4C_{18})]^3\left(\frac{\rho g v}{\sigma}\right) Re_L^{3(1-m)}. \tag{27}$$

Hence for this equation $k_L \propto Re_L^{3(1-m)/2}$. The results obtained for a and k_L are summarized in Table 3.

Experimental data show that $\bar{k}_L$ depends on the film Reynolds number, Re_L, raised to a power from 0.55 to 1.14 for the turbulent region of the flow [3, 4, 7, 11, 22, 27–34]. Most of the data concern mass transfer into water and for this system the power exponent at Re_L has been found to be in the range of 0.57–0.84. The values of the exponent close to 0.82–0.85 have been obtained by Won and Mills [28] for absorption of CO_2, O_2 and H_2 by ethanol. However, considerably lower values have been noted by these authors in the case of CO_2 absorption by methanol (0.546). For propanol aqueous solutions and ethylene glycol–water mixtures the power exponent at Re_L has been found to increase from 0.75 to 1.14 with increasing concentration of the organic components [27, 28]. These authors attempted to account for the influence of the liquid phase properties on mass transfer coefficients into a turbulent falling film flow and proposed an empirical correlation revealing the effect of the basic liquid phase properties on the power exponents at both film Reynolds and Schmidt numbers. However, their conclusion is not confirmed by the data of Gildenblat *et al.* [32] obtained for desorption of CO_2 and He from heptane which show that $k_L \propto Re_L^{0.77}$ and the power exponent at Sc, $n = 0.52$–0.58.

A comparison of experimentally found values of the exponent at Re_L with those resulting from the models listed in Table 3 shows that the Levich–Davies and King models, after substitution of v_0 and $\bar{\varepsilon}$ as indicated, yield significantly lower power exponents at Re_L. Thus, it can be assumed that these models will fail to adequately predict mass transfer coefficients for the

Table 3. Different models' predictions for a and k_L

Author	$a \propto$	$a \propto$ for $m = 0.526$	$\bar{k}_L \propto$	$\bar{k}_L \propto$ for $m = 0.526$
Levich–Davies	$Re_L^{3m/2}$	$Re_L^{0.789}$	$Re_L^{3m/4}$	$Re_L^{0.395}$
King	$Re_L^{(1-m)/2}$	$Re_L^{0.237}$	$Re_L^{(1-m)/4}$	$Re_L^{0.12}$
Prasher	$Re_L^{3/2}$	$Re_L^{3/2}$	$Re_L^{3/4}$	$Re_L^{3/4}$
Kishinevskiy	$Re_L^{3(1-m)}$	$Re_L^{1.422}$	$Re_L^{3(1-m)/2}$	$Re_L^{0.711}$
Carrubba	$Re_L^{2.50-2m}$	$Re_L^{1.448}$	$Re_L^{1.25-m}$	$Re_L^{0.724}$
Henstock	$Re_L^{5m/2}$	$Re_L^{1.315}$	$Re_L^{5m/4}$	$Re_L^{0.658}$

turbulent falling liquid films if simple relationships for v_0 and $\bar{\varepsilon}$ are to be used. Among the remaining four models, at this stage, one cannot definitely choose the best one, although the power exponent at Re_L for the model of Prasher and Fricke seems to be the best fit to the experimental findings and since it does not depend on the exponent m describing the average film thickness. However, it must be emphasized that the above given considerations take into account only the basic (macroscopic) hydrodynamic properties of the falling films and neglect the complicated nature of the wavy flow in such films. As has been pointed out by Henstock and Hanratty [7], at present it is still not possible to distinguish from the available measurements whether waves or turbulence are the controlling factors for the mass transfer since not much is known about the damped region of turbulence close to the interface.

So far the only available experimental data on the turbulence characteristics in turbulent films flowing down an inclined smooth plate are due to Lozano [37, 38]. The author used a hot-wire anemometer and from the measurements carried out at $y = 0.5$ mm he estimated different velocity and length scales at two film Reynolds numbers, 4000 and 5200. It follows from his data that the ratio of the root mean square fluctuation velocity in the x direction, $\tilde{v}_x'$, to the friction velocity, v^*, is 1.19 for $Re_L = 4000$ and 2.37 for $Re_L = 5200$. The macroscale length l_L (comparable to energy containing eddy length) is 42 mm for $Re_L = 4000$ and 23 mm for $Re_L = 5200$, whilst the average film thicknesses are of the order of 1 mm. Similarly the microscale length l_m (comparable to energy dissipating eddy length) has a value of approximately 5 mm for both Re_L values studied. The rate of energy dissipation has been calculated by the author [37] from the relation

$$\varepsilon = \tilde{v}_x'^3 / l_L \tag{28}$$

divided by the correction factor $[1 + 5(\tilde{v}_x'/\bar{v}_x)^2]$ suggested by Lumley [39].

Although the turbulence data collected by Lozano [37] for a smooth plate are very scarce they indicate that the actual turbulence scales, $\tilde{v}_x'$ and l_m or l_L, differ significantly from those simply assumed as corresponding to v^* or δ [3, 7]. Also, the 'local' values of the rate of energy dissipation, ε, differ largely from the average values of $\bar{\varepsilon}$ calculated from equation (21). The largest x directional eddies contain about 60% of the turbulent energy but they do not apparently control mass transfer rates. The authors [37, 38] conclude that the eddies responsible for mass transfer are intermediate in size between the x directional and the y directional large eddies.

Since the scope of the experimental data on turbulence characteristics of turbulent film flows is very limited it is still not possible to establish more conclusive links between the parameter a and the turbulence parameters of the film. Therefore, the only remaining way is an indirect comparison with the mass transfer data.

DISCUSSION

The turbulent region of the falling liquid film extends above approximately $Re_L \geqslant 1600$. There are a number of experimental data on mass transfer for this region available in the literature [4, 7, 11, 22, 27–34]. In view of the earlier discussion it is important to choose data that have been collected for fully-developed concentration profiles. For such data, equation (5) may be used to obtain a dependence of the parameter a on the film parameters via the mass transfer coefficients.

Lamourelle and Sandall [4] used three different column lengths, 0.914, 1.372 and 1.83 m, and found no effect of the column length on mass transfer coefficients. Hence, one can conclude that the column at least 1 m long should provide conditions sufficient to ensure fully-developed concentration profiles. Besides, flow development zones and the incipience of wavy flow may have some effect on mass transfer (cf. [34–36]). These effects depend largely on the geometry of the column and in particular on the liquid distribution devices [34]. Inspection of the geometry of falling film equipment used by different authors indicates that mass transfer coefficients are not affected by the ratio L/d when it is higher than about 50. This is in contrast to the recent finding of Bakopoulos [34] who established the critical ratio of L/d equal to 156 for his distribution device. However, this author also concludes that the column lengths greater than about 1 m will provide fully-developed turbulent film flow.

These conclusions can be verified by comparing them with the previously made conclusion ($X \geqslant 20$ to attain a long contact time asymptote) after establishing the numerical values of a.

It can be seen that equations (23), (24), (25) and (27) can be grouped by noting the fact that equations (23) and (27) are similar, and correspondingly, equations (24) and (25) are also similar, differing only in the power exponents and the constants. However, if these two groups of the empirical equations for a are compared, they differ significantly in physical liquid properties terms, the first group having the term $(\rho g v/\sigma)$ whereas the latter have the term $(g^2/v)^{1/3}$. Thus, the surface tension effect is not accounted for in equations (24) and (25). The authors of the subsequent empirical equations fitted them to the experimental data of different authors collected exclusively for water systems with different gases used in mass transfer experiments. Also, the majority of these data pertain to the temperature of 25°C.

Figures 1–4 present the results of such fitting procedures for the two types of the empirical correlations. About 520 data points given by different authors have been used. Table 4 lists basic information on the systems studied and the flow configuration.

For the water systems (Figs. 1 and 3) both types of correlations show approximately the same scatter around the best line. For the pure organic solvents, in the case of the Prasher and Fricke correlation, Fig. 2, the majority of the data points due to Won and Mills

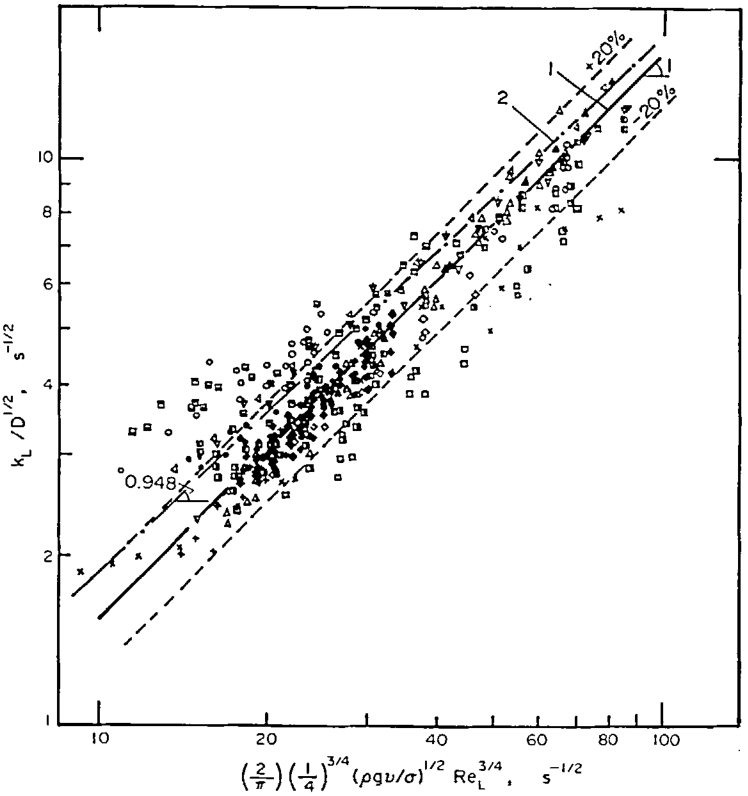

FIG. 1. Correlation of $\bar{k}_L/D^{1/2}$ vs $(2/\pi)(1/4)^{3/4}(\rho g v/\sigma)^{1/2}\,Re_L^{3/4}$ for water systems. (1) equations (5) and (23) with $n = 2$ and $C_{23} = 0.024$; (2) equations (5) and (27) with $n = 2, m = 0.526$ and $C_{14} = 15$. Symbols are explained in Table 4.

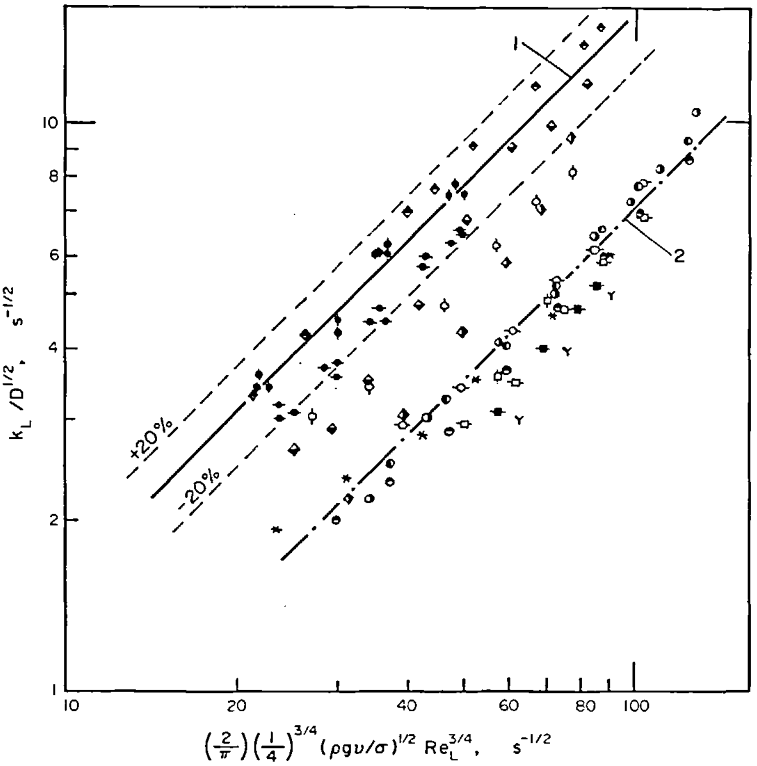

FIG. 2. Correlation of $\bar{k}_L/D^{1/2}$ vs $(2/\pi)(1/4)^{3/4}(\rho g v/\sigma)^{1/2}\,Re_L^{3/4}$ for organic liquid systems. (1) equations (5) and (23) with $n = 2$ and $C_{23} = 0.024$; (2) equations (5) and (23) with $n = 2$ and $C_{23} = 0.0050$. Symbols are explained in Table 4.

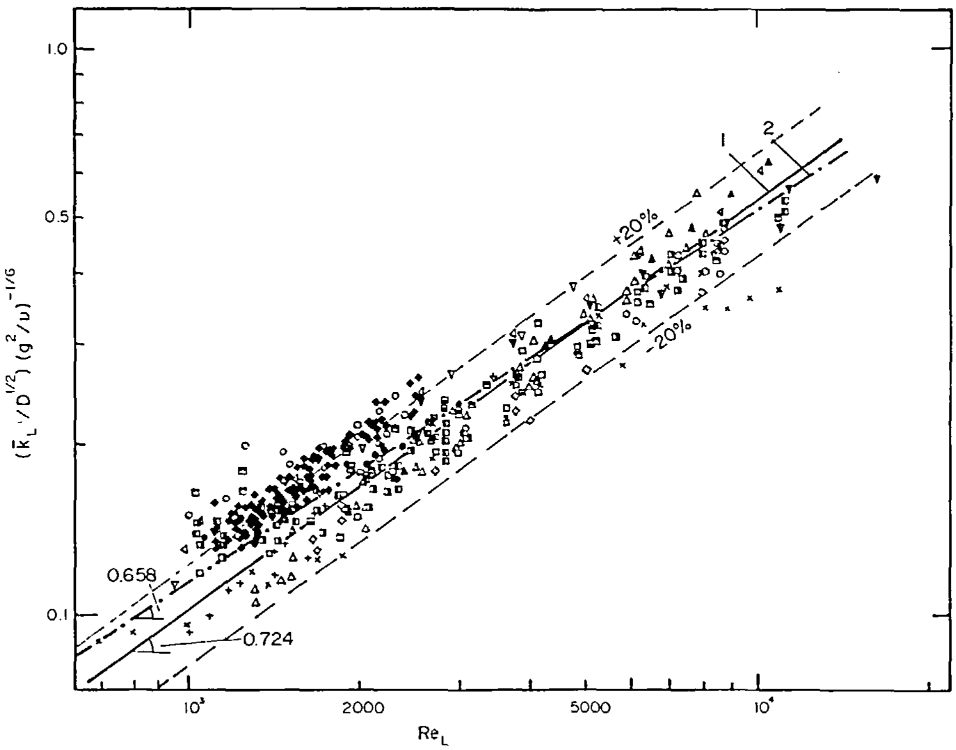

FIG. 3. Correlation of $(\bar{k}_L/D^{1/2})(g^2/\nu)^{1/6}$ vs Re_L for water systems. (1) equations (5) and (24) with $n = 2$, $m = 0.526$ and $C_{15} = 6.09 \times 10^{-8}$; (2) equations (5) and (25) with $n = 2$, $m = 0.526$ and $C_{25} = 1.463 \times 10^{-4}$. Symbols are explained in Table 4.

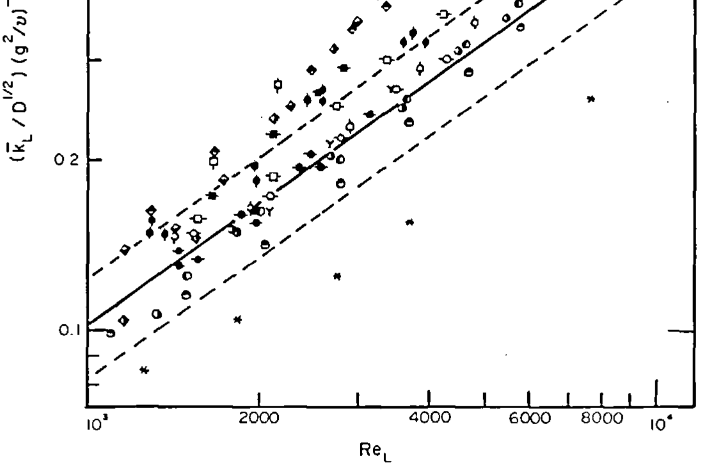

FIG. 4. Correlation of $(\bar{k}_L/D^{1/2})(g^2/\nu)^{1/6}$ vs Re_L for organic liquid systems. (1) equations (5) and (24) with $n = 2$, $m = 0.526$ and $C_{15} = 6.09 \times 10^{-8}$. Symbols are explained in Table 4.

Table 4. Experimental conditions

Authors	Flow configuration length (m)	diameter (mm)	System Solute	Solvent	Temp. (°C)	Symbol
Kamei and Oishi [22]	2.5	47.6	CO_2	Water	8.5	□
					14	◨
					25	◧
					35	⬒
					50	⬓
Emmert and Pigford [29]	1.137	25.4	CO_2 O_2	Water		+
Davies and Warner [30]	0.81	Plate	CO_2	Water	25	◇
Lamourelle and Sandall [4]	1.83	15.9	CO_2, O_2, H_2, He	Water	25	△
Menez and Sandall [11]	1.83	15.9	CO_2	Water	25	▲
Coeuret *et al.* [31]	Not reported	4.0	CO_2	Water	30	○
Broniarz [33]	1.5	29.7 37.6 49.0	CO_2	Water	8.5–11	◆
Chung and Mills [27]	1.98	20.5	CO_2	Dist. water	25	◁
				Tap water	14	▽
					25	▼
					40	⍒
Bakopoulos [34]	2.983	19.1	CO_2	Water	26	●
Henstock and Hanratty [7]	0.9–2.1	25.4	O_2	Water		×
Gildenblat *et al.* [32]	1.04	20.0	He	Heptane	20	●̍
			CO_2	Heptane	20	-●-
Chung and Mills [27]	1.98	20.5	CO_2	5.2% EG†	25	⬘
			CO_2	12% EG	25	⬙
			CO_2	20% EG	25	⬗
Won and Mills [28]	1.98	20.5	CO_2	Methanol	25	✱
			CO_2	Ethanol	25	◑
			CO_2	Propanol	25	Y
			O_2	Ethanol	25	◐
			H_2	Ethanol	25	◓
			CO_2	2% PR‡	25	⌽
			CO_2	5% PR	25	⊖
			CO_2	10% PR	25	⊟
			CO_2	20% PR	25	◫
			CO_2	50% PR	25	-■-

† EG—ethylene glycol solution with water.
‡ PR—propanol solution with water.

[28] deviate from the best line obtained for the water systems. However, data given by Gildenblat *et al.* [32] for heptane are adequately represented by the line obtained for the water systems. Data points corresponding to the aqueous solutions of ethylene glycol and propanol deviate from the water systems best line and lie between the water and pure organic solvents lines.

Figure 4 presents data points for organic solvents in coordinates $\bar{k}_L/D^{1/2}(g^2/\nu)^{1/6}$ vs Re_L. This type of correlation seems to yield a better fit for all systems studied. Greater deviations (up to +75%) are seen for the aqueous ethylene glycol solutions and for methanol (up to −41%). Possible reasons for these discrepancies are (i) interfacial turbulence in the case of aqueous solutions, (ii) different wavy film structure in the case of aqueous solutions in comparison with pure liquids, and (iii) inaccuracies in diffusivity coefficients given by the authors [28].

Not much can be stated on the two first possible effects. However, there is some experimental evidence that in the case of solutions, desorption of one of the liquid-phase components may enhance the mass transfer coefficients [40] because of Marangoni instability. The third reason seems to be evidenced by comparing the value of $D_{CO_2} = 8.37 \times 10^{-9}$ m^2 s^{-1} given by the authors [28] for methanol at 25°C with those resulting from some empirical equations [41, 42, 44]. The most probable value would be $D_{CO_2} = 5 \times 10^{-9}$ m^2 s^{-1} at 25°C and for such a value data points for methanol would deviate from the best fit for water and pure organic solvents by a maximum of −25%.

Thus, from a direct comparison of the two types of the empirical correlations for the eddy diffusivity parameter with mass transfer data, one can conclude that ignoring the effect of surface tension gives better agreement with experiments for all systems studied, covering the following range of the basic liquid-phase physical properties: kinematic viscosity from 0.55×10^{-6} to 2.88×10^{-6} m^2 s^{-1}, surface tension from 0.021 to 0.0735 N m^{-1}, density from 785 to 1050 kg m^{-3}, and Schmidt number from 25 to 2700. Also Gildenblat *et al.* [32] concluded that in the case of absorption into a turbulent free liquid surface, there is no effect of surface tension on the value of power exponent at D, whereas Theofanous *et al.* [43] suggested that the effect of surface tension on mass transfer coefficient should be relatively small for the case of turbulent mass transfer.

Therefore, equation (24) due to Carrubba [6] can be recommended as the most reliable. If the constants $C_{18} = 0.228$ and $m = 0.526$ are chosen, then for $C_{15} = 6.09 \times 10^{-8}$ equation (24) reads

$$a = 1.17 \times 10^{-6}(g^2/\nu)^{1/3} Re_L^{1.448}. \qquad (29)$$

The values of a calculated from equation (24) by using the values of C_{18} and m given by other authors do not differ much from the values resulting from equation (29); they are usually in the range of ±15%. Equation (25) due to Henstock and Hanratty [7], with $C_{25} = 1.463 \times 10^{-4}$ resulting from the authors' original correlation, and C_{18} and m according to Takashima and Kato gives results differing by +23% at $Re_L = 1000$ and by −14% at $Re_L = 15\,000$ from those calculated from equation (29).

An empirical equation correlating the mass transfer coefficients with liquid-phase properties, recently attempted by Won and Mills [28], gives most frequently greater deviation from the experimental data of the other authors though it is more complicated and predicts some variation of the power exponent at the film Reynolds number.

Having established an empirical correlation for the eddy diffusivity parameter, equation (29), it is now possible to check more formally the validity of the previously made assumption of sufficiently long contact times, equation (6), for the data points considered. Figure 5 presents the results of such a check. The values of X have been calculated by using equation (29) for a, equation (20) with $C_{20} = 1.3$ for the film surface velocity, equations (18) and (19) with $C_{18} = 0.228$ and $m = 0.526$ for the mean film thickness and the mean film velocity, respectively. The same expressions have been used to calculate the values of Ψ_m. It can be seen that practically all data points considered in Figs. 1–4 correspond to the values of $X \geqslant 20$. The agreement with the long time asymptote, equation (6), is, as can be expected, within the same range of accuracy as equation (29). Larger deviations are repeatedly observed for the aqueous ethylene glycol solutions and for methanol.

CONCLUDING REMARKS

The eddy diffusivity model under the assumption of $n = 2$ seems to adequately describe mass transfer into turbulent film flow. Among a few empirical attempts to correlate the eddy diffusivity parameter with the liquid-

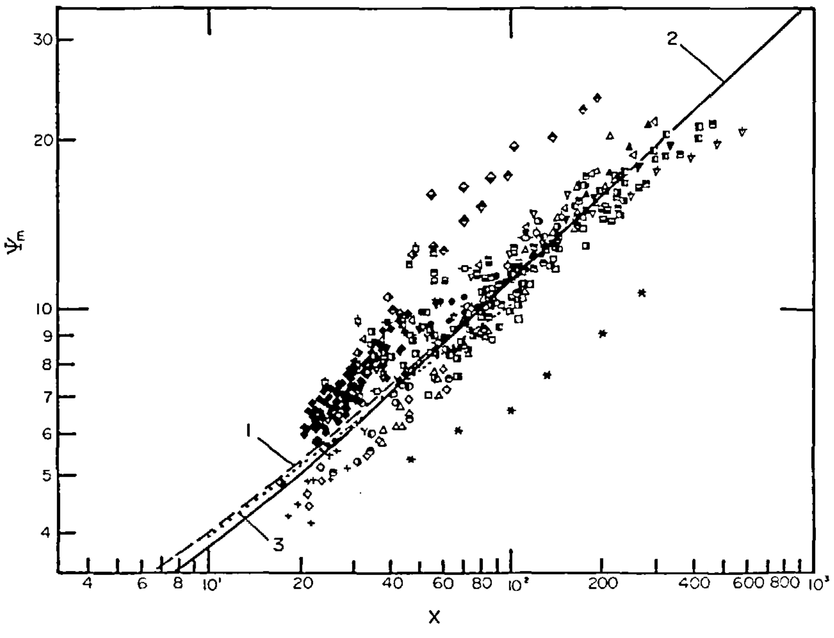

FIG. 5. Comparison of theoretical dependence of Ψ_m on X with the experimental data. (1) according to Kishinevskiy and Korniyenko [18]; (2) according to Gottifredi and Quiroga [13]; (3) according to Yih and Seagrave [14]. Symbols are explained in Table 4.

phase properties obtained from Carrubba's [6] suggestion, equation (29), gives the best agreement with experimental data of many authors collected for different gas–liquid systems. Greater deviations from this equation are noted for the aqueous solutions of ethylene glycol and propanol and for methanol, probably due to possible effects of interfacial turbulence, different wavy structure and inaccuracies in molecular diffusion coefficients. Surface tension does not seem to affect mass transfer coefficients in turbulent film flows.

Because of a scarcity of experimental data on turbulence characteristics in turbulent liquid film flows, it is not yet possible to establish direct links between turbulence and mass transfer coefficients. Also, a few attempts to consider wavy structure of the turbulent falling films have not yielded more convincing conclusions concerning mass transfer coefficients.

REFERENCES

1. V. G. Levich, *Physicochemical Hydrodynamics*. Prentice-Hall, Englewood Cliffs, New Jersey (1962).
2. C. J. King, Turbulent liquid phase mass transfer at a free gas–liquid interface, *I/EC Fundamentals* **5**, 1–8 (1966).
3. J. T. Davies, *Turbulence Phenomena*. Academic Press, New York (1972).
4. A. P. Lamourelle and O. C. Sandall, Gas absorption into a turbulent liquid, *Chem. Engng Sci.* **27**, 1035–1043 (1972).
5. B. D. Prasher and A. L. Fricke, Mass transfer at a free gas–liquid interface in turbulent thin films, *I/EC Process Des. Dev.* **13**, 336–340 (1974).
6. G. Carrubba, Stoff- und Wärmetransport im welligen Riesel film, Ph.D. thesis, Technische Universität Berlin (1976).
7. W. H. Henstock and T. J. Hanratty, Gas absorption by a liquid layer flowing on the wall of a pipe, *A.I.Ch.E. Jl* **25**, 122–131 (1979).
8. S. Banerjee, D. S. Scott and E. Rhodes, Mass transfer to falling wavy liquid films in turbulent flow, *I/EC Fundamentals* **7**, 22–27 (1968).
9. J. C. Lamont and D. S. Scott, An eddy cell model of mass transfer into the surface of a turbulent liquid, *A.I.Ch.E. Jl* **16**, 513–519 (1970).
10. L. K. Brumfield, R. N. Houze and T. G. Theofanous, Turbulent mass transfer at free, gas–liquid interfaces, with applications to film flows, *Int. J. Heat Mass Transfer* **18**, 1077–1081 (1975).
11. G. D. Menez and O. C. Sandall, Gas absorption accompanied by first-order chemical reaction in turbulent liquids, *I/EC Fundamentals* **13**, 72–76 (1974).
12. J. B. Stepanek and S. K. Achwal, Absorption with first order chemical reaction into turbulently flowing liquids, *Can. J. Chem. Engng* **53**, 517–520 (1975).
13. J. C. Gottifredi and O. D. Quiroga, Gas absorption into a turbulent falling film, *Chem. Engng Jl* **16**, 199–204 (1975).
14. S. M. Yih and R. C. Seagrave, An analytical solution for mass transfer in turbulent falling films with and without chemical reaction, *Chem. Engng Sci.* **33**, 1581–1587 (1978).
15. J. C. Gottifredi and O. D. Quiroga, Gas absorption accompanied by first-order reversible and irreversible reactions in turbulent liquid films, *Int. J. Heat Mass Transfer* **22**, 839–847 (1979).
16. O. C. Sandall, Gas absorption into turbulent liquids at intermediate contact times, *Int. J. Heat Mass Transfer* **17**, 459–461 (1974).
17. R. S. Subramanian, Gas absorption into a turbulent liquid film, *Int. J. Heat Mass Transfer* **18**, 334–336 (1975).
18. M. Kh. Kishinevskiy and T. S. Korniyenko, Mass transfer in systems with a deformable interface, *Zh. Prikl. Khim.* **50**, 2520–2524 (1977).
19. W. Brötz, Über die Vorausberechnung der Absorptionsgeschwindigkeit von Gasen in strömenden Flüssigkeitsschichten, *Chemie–Ingr–Tech.* **26**, 470–478 (1954).
20. H. Brauer, Strömung und Wärmeübergang bei Rieselfilmen, *VDI-Forsch.* 457 (1956).
21. K. Feind, Strömungs Untersuchungen bei Gegenstrom von Rieselfilmen und lotrechten Rohren, *VDI-Forsch.* 481 (1960).
22. S. Kamei and J. Oishi, Mass and heat transfer in a falling liquid film of wetted tower, *Mem. Fac. Engng Kyoto Univ.* **17**, 277–280 (1955).
23. L. Y. Zhivaykin and B. P. Volgin, Liquid flow on a vertical surface, *Zh. Prikl. Khim.* **34**, 1236–1239 (1961).
24. H. Ueda, R. Möller, S. Komori and T. Mizushina, Eddy diffusivity near the free surface of open channel flow, *Int. J. Heat Mass Transfer* **20**, 1127–1136 (1977).
25. H. Takahama and S. Kato, Longitudinal flow characteristics of vertically falling liquid films without concurrent gas flow, *Int. J. Multiphase Flow* **6**, 203–215 (1980).
26. A. S. Telles and A. E. Dukler, Statistical characteristics of thin, vertical, wavy liquid films, *I/EC Fundamentals* **9**, 412–421 (1970).
27. D. K. Chung and A. F. Mills, Experimental study of gas absorption into turbulent falling films of water and ethylene glycol–water mixtures, *Int. J. Heat Mass Transfer* **19**, 51–59 (1976).
28. Y. S. Won and A. F. Mills, Correlation of the effects of viscosity and surface tension on gas absorption rates into freely falling turbulent liquid films, *Int. J. Heat Mass Transfer* **25**, 223–229 (1982).
29. R. E. Emmert and R. L. Pigford, A study of gas absorption in falling liquid films, *Chem. Engng Prog.* **50**, 87–93 (1954).
30. J. T. Davies and K. V. Warner, The effect of large-scale roughness in promoting gas absorption, *Chem. Engng Sci.* **24**, 231–240 (1969).
31. F. Coeuret, B. Jamet and J. J. Ronco, Transfert de matiére avec et sans reaction chimique dans un film tombant cylindrique en régime de transitions et en régime turbulent, *Chem. Engng Sci.* **25**, 17–21 (1970).
32. I. A. Gildenblat, A. I. Rodionov and B. I. Demchenko, On the effect of molecular diffusivity on mass transfer between gases and liquids of different surface tensions and viscosities, *Dokl. Acad. Sci. U.S.S.R.* **198**, 1149–1151 (1971).
33. L. Broniarz, Investigation of the effect of surface roughness on mass transfer in liquid phase, Ph.D. thesis, Poznań Technical University (1977).
34. A. Bakopoulos, Liquid-side controlled mass transfer in wetted-wall tubes, *German Chem. Engng* **3**, 241–252 (1980).
35. L. P. Kholpanov, V. Y. Shkadov, V. A. Malusov and N. M. Zhavoronkov, Studies of hydrodynamics and mass transfer in a film flow with accounting for the inlet section, *Teor. Osn. Khim. Tekhn.* **10**, 659–669 (1976).
36. L. P. Kholpanov, V. A. Malusov and N. M. Zhavoronkov, Hydrodynamics and mass transfer in turbulent liquid film flow involving the inlet portion, *Coll. Czech. Chem. Comm.* **46**, 467–477 (1981).
37. F. J. Lozano, Turbulence and mass transfer, Ph.D. thesis, University of Birmingham (1976).
38. J. T. Davies and F. J. Lozano, Turbulence characteristics and mass transfer at air–water surfaces, *A.I.Ch.E. Jl* **25**, 405–415 (1979).
39. J. L. Lumley, Interpretation of time spectra measured in high-intensity shear flows, *Physics Fluids* **8**, 1056–1060 (1965).
40. K. Fujinawa, M. Hozawa and N. Imaishi, Effects of desorption and absorption of surface tension-lowering

solutes on liquid-phase mass transfer coefficients at a turbulent gas–liquid interface, *J. Chem. Engng Japan* **11**, 107–111 (1978).

41. W. Hayduk and S. C. Cheng, Review of relation between diffusivity and solvent viscosity in dilute liquid solutions, *Chem. Engng Sci.* **26**, 635–646 (1971).
42. H. Sovova, Correlation of diffusivities of gases in liquids, *Coll. Czech. Chem. Comm.* **41**, 3715–3722 (1976).
43. T. G. Theofanous, R. N. Houze and L. K. Brumfield, Turbulent mass transfer at free, gas–liquid interfaces, with applications to open-channel, bubble and jet flows, *Int. J. Heat Mass Transfer* **19**, 613–623 (1976).
44. M. Takahashi, Y. Kobayashi and H. Takeuchi, Diffusion coefficients and solubilities of CO_2 in binary solvents, *J. Chem. Engng Data* **27**, 328–331 (1982).

TRANSFERT MASSIQUE DANS UN FILM LIQUIDE TURBULENT

Résumé—Différents essais d'application du modèle de la diffusivité turbulente à la description du transfert massique dans un film liquide tombant ont été rassemblés et comparés. L'attention est principalement portée sur le domaine d'applicabilité du modèle et sur ses faiblesses en prenant en considération les propriétés physiques et hydrodynamiques des systèmes étudiés. On montre que la tension superficielle n'affecte pas les coefficients de transfert massique.

STOFFÜBERGANG IN EINEN TURBULENTEN FLÜSSIGKEITSFILM

Zusammenfassung—Die Versuche verschiedener Autoren, das Wirbeldiffusionsmodell für die Beschreibung des Stoffübergangs in einen turbulenten Rieselfilm anzuwenden, wurden durchgesehen und verglichen. Besondere Aufmerksamkeit wurde dabei auf den Anwendungsbereich der Modelle und ihren Zusammenhang mit den grundlegenden, physikalischen und hydrodynamischen Eigenschaften der untersuchten Systeme verwendet.

Es wird gezeigt, daß die Oberflächenspannung den Stoffübergangskoeffizienten nicht beeinflußt.

МАССОПЕРЕНОС В ТУРБУЛЕНТНУЮ ПЛЕНКУ ЖИДКОСТИ

Аннотация—Дан обзор и проведено сравнение попыток применения различными авторами модели вихревой диффузии для описания массопереноса в турбулентной стекающей пленке жидкости. Основное внимание обращено на область применимости модели и ее связь с основными физическими и гидродинамическими параметрами исследуемых систем. Показано, что поверхностное натяжение не оказывает влияния на коэффициенты массопереноса.