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Physical and hydrodynamical parameters controlling gas–liquid mass transfer

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Abstract—Turbulence measurements carried out in a vessel, in which turbulence was produced by means of upflowing microjets of water, with zero mean shear stress at the interface, show that the turbulent kinetic energy level is increased close to the interface where horizontal eddies develop. Gas absorption experiments carried out simultaneously show that the interfacial turbulence level and the gas absorption coefficient are closely related. In the same conditions, velocity power density spectra show a development of the lower frequencies in the horizontal direction. When a surfactant (Hexadecanol) is added, interfacial mass transfer is reduced while the existing horizontal velocity fluctuations are relatively damped. There, the interface behaves more like a solid wall than like a free surface.

INTRODUCTION

THE KNOWLEDGE of gas–liquid mass transfer at water surfaces is of great importance in the environment (aeration of lakes, ocean–atmosphere exchanges, treatment of gaseous effluents by liquid cleaners) and in chemical or biochemical engineering (improvement of reactors).

Concerning interfacial absorption of weakly soluble gases, for which resistance to transfer takes place inside the liquid phase, the mass transfer prediction depends on the modelling of the dynamic interfacial phenomena.

Most conceptual models found in the literature are based either on the stagnant film model (Whitman [1]: $K_L = D_\mu/l$ where l is the diffusive film thickness at the interface) or on the surface renewal model (Danckwerts [2]: $K_L = \sqrt{(D_\mu s)}$ where s is the characteristic renewal frequency). They consist in the determination of l or s by introducing the effective diffusivity concept (Levich [3]) or by determining the size of the most efficient eddies (large eddies according to Fortescue and Pearson [4] or dissipative structures for Lamont and Scott [5]).

All models can be written in a non-dimensional form (Aïsa *et al.* [6]):

$$\frac{K_L}{u_0} = f(D_\mu, \rho_L, \nu_L, \sigma, l_0, \varepsilon) \propto Sc^n Re^p We^q$$

where u_0 is a characteristic velocity, D_μ, ρ_L, ν_L, σ are physical parameters, l_0 is a length scale and ε the dissipation rate. The non-dimensional numbers appearing in this relation are the Reynolds number ($Re = u_0 l_0/\nu_L$), the Schmidt number ($Sc = \nu_L/D_\mu$) and the Weber number ($We = \rho_L l_0 {u_0}^2/\sigma$). The respective values of n, p and q are:

$$n = -1/2 \text{ or } -2/3 \quad p = -1/2, -1/4 \text{ or } +1/2$$
$$\text{and} \quad q = 0 \text{ or } +1/2.$$

More recently, Hanratty [7] proposed the following relation (for gas–liquid flows in channels):

$$K_L/u_{SL} = 0.12\, Sc^{-1/2} \text{ (for } \tau_I/\tau_w > 0.3 \text{ and } h^+ > 40) \tag{1}$$

in which $u_0 = u_{SL}$ is the interfacial liquid friction velocity ($u_{SL} = \sqrt{(\tau_I/\rho_L)}$) and where τ_I, τ_w and h^+ are, respectively, the interfacial gas–liquid stress, the friction at the bottom wall and the non-dimensional depth relative to u_{SL} and to the liquid kinematic viscosity ν_L ($h^+ = hu_{SL}/\nu_L$).

Unfortunately, the use of u_{SL} as a characteristic velocity scaling does not permit a correct prediction of situations:

- for which there is no mean shear stress (stirred vessels, vessels agitated by oscillating grids or upflowing jets (Grisenti and George [8]));
- for which there exist large developing waves (Caussade *et al.* [9]). At sea, it has been shown (Kitaigorodskii *et al.* [10]) that the ratio k_I/u_{SL}^2 could reach approximately 50 when it ranges between 3 and 16 for small fetches;
- for which wall turbulence directly governs interfacial turbulence (free falling films—Henstock and Hanratty [11]).

In order to get a velocity scale u_0 representative of

NOMENCLATURE

A	free surface area of the quiescent liquid [m^2]
Am	Hexadecanol molecular area [m^2]
$Ce\ (t)$	input concentration (time dependent) [g m^{-3}]
C_s	interfacial concentration [g m^{-3}]
$\langle C(t) \rangle$	bulk concentration (time dependent) [g m^{-3}]
D_g	molecular gas diffusivity in the liquid [m^2 s^{-1}]
h	liquid depth [m]
h^+	normalized liquid depth, hu_{SL}/ν_L
J	mass transfer flux [kg s^{-1}]
K_L	gas absorption coefficient at the interface [m s^{-1}]
$K_L A$	volumetric gas absorption coefficient [m^3 s^{-1}]
k	turbulent kinetic energy [m^2 s^{-2}]
k_I	interfacial kinetic energy [m^2 s^{-2}]
l	diffusive film thickness [m]
l_0	characteristic length scale [m]
q_L	liquid flow-rate [m^3 s^{-1}]
Re	Reynolds number, $u_0 l_0/\nu_L$
s	surface renewal frequency [m^2 s^{-1}]
Sc	Schmidt number ν_L/D_g
t	time [s]
U, V	mean horizontal velocity components [m s^{-1}]
u_0	characteristic velocity scale [m s^{-1}]
u', v'	instantaneous horizontal velocity fluctuations in U, V directions [m s^{-1}]
u_R, w_R	relative RMS velocity, $u_R = \sqrt{(\overline{u'^2})}/\sqrt{(k)}$, $w_R = \sqrt{(\overline{w'^2})}/\sqrt{(k)}$
u_N	normalized RMS horizontal velocity, $\sqrt{(\bar{u}'^2)}/\sqrt{(\bar{u}'^2_{MIN})}$
u_{SL}	interfacial friction velocity [m s^{-1}]
W	mean vertical velocity component [m s^{-1}]
w'	instantaneous vertical velocity fluctuation [m s^{-1}]
We	Weber number, $\rho_L l_0 u_0{}^2/\sigma$
x, y	horizontal co-ordinates [m]
z	vertical co-ordinate [m]
z_S	distance of the virtual origin from the average free surface position [m].

Greek symbols

δ	local distance to the virtual origin [m]
δ_R	relative distance to the virtual origin δ/δ_S
δ_S	distance between the interface and the virtual origin [m]
ε	dissipation rate [m^2 s^{-3}]
θ	temperature [°C]
ν_L	liquid kinematic viscosity[m^{-2} s^{-1}]
ρ_L	liquid density [kg m^{-3}]
σ	surface tension [N m^{-1}]
τ_I	interfacial shear stress [N m^{-2}]
τ_w	wall friction[N m^{-2}]

Other symbols

—	time average value
$\langle\,\rangle$	spatial average value

a broad range of mass transfer conditions, Asher and Pankow [12] proposed the use of $(\varepsilon/\nu)^{1/4}$ as characteristic velocity u_0. From this, they showed it was possible to relate stirred tank results to wind tunnel experiments provided the aqueous surface is clean. Our approach is somewhat different, the idea being the study of the role of interfacial turbulence level, the importance of which was anticipated by Caussade *et al.* [9]. Therefore a jet-agitated vessel with no mean shear stress at the interface was built. In this agitated box, turbulence generated by upflowing jets is almost isotropic in the bulk region relatively far away from the jet nozzles and from the surface (in that region turbulence can be considered as homogeneous in the horizontal plane). Interfacial velocity fluctuations were measured and it was shown that the mass transfer rate is related with the turbulent kinetic energy k_I present at the interface (Grisenti and George [8]).

Thus $\sqrt{(k_I)}$ can be chosen as characteristic velocity u_0 and in all situations listed above, as was shown by Magnaudet *et al.* [13], mass transfer rate at a clean interface ranges between:

$$0.028\,Sc^n \leqslant K_L/\sqrt{(k_I)} \leqslant 0.056\,Sc^n \qquad (2)$$

where n, the Schmidt number exponent, can vary from $-2/3$ to $-1/2$ depending on the surface agitation level.

Hence, the non-dimensional mass transfer rate can be modelled by (Grisenti and George [8]):

$$K_L/\sqrt{(k_I)} = 0.03\,Sc^n. \qquad (3)$$

Relations (1) and (3) are in rather good agreement since u_{SL} ranges, in the absence of large developing waves, between:

$$3 < k_I/u_{SL}^2 < 16. \qquad (4)$$

In the present study, the interest is focused on the role played by a surface active agent, through experiments with and without surfactants: that is, on the role played by interfacial two-dimensional eddies in which they are allowed or not allowed to develop freely.

The discussion of new experimental results, including K_L measurements in the presence of Hexadecanol, is presented after a brief description of the jet-agitated vessel and the recall of previous results.

EXPERIMENTAL STUDIES

Apparatus and procedure

Carbon dioxide absorption experiments and liquid phase turbulence studies were conducted in the jet-agitated vessel described in detail by Grisenti [14].

The vessel consists of an Altuglass tank, with a square (0.45×0.45 m^2) bottom and a height of 0.80 m. The square base was used in order to prevent the occurrence of preferential flows, in particular mean rotating flows (Fig. 1).

An array of one hundred microjet nozzles (0.7×10^{-3} m in diameter) is built in an injection–evacuation device (Fig. 2). The jet nozzles are regularly distributed in the injection plane and are separated from each other by 4.3×10^{-2} m in each direction.

The microjet input velocity varied between 5 and 15 meters per second.

The liquid depth in the vessel is maintained constant using a constant head tank which allows the interfacial turbulence level to be adjusted.

The liquid phase velocity is measured using a Laser Doppler Velocimeter (LDV). A Bragg cell is added in order to permit velocity measurements in the absence of mean movements. The LDV output is connected to a HP 1000 computer through an LMS data processing system.

Properties of horizontal and vertical velocity components were analyzed. These include the average mean velocities, the RMS fluctuations and the power density spectra.

Bulk carbon dioxide concentrations $\langle C(t) \rangle$ are measured by following, in the liquid phase, the time variations of conductimetry of initially deionized water.

Pure deionized water is used in order to lower the initial conductivity of water without CO_2 but also to prevent particles of dust from contaminating the free surface. For this reason the vessel was covered by a Plexiglas lid.

The interfacial carbon dioxide concentration C_S is given by Henry's law from measurements of carbon dioxide concentrations in the gaseous phase, using an infrared analyser.

Bulk temperature θ inside the liquid phase is measured by a thermocouple.

Concentration and temperature values are recorded on a PM 8237 Philips multipoint data recorder.

Analysis of data

As it is shown in Fig. 3, the absorption flux $J = K_L A (C_S - \langle C(t) \rangle)$ corresponds to an enhancement of the bulk concentration $\langle C(t) \rangle$ when C_S is maintained constant.

The mass balance equation for the tracer gives (Grisenti and George [8]):

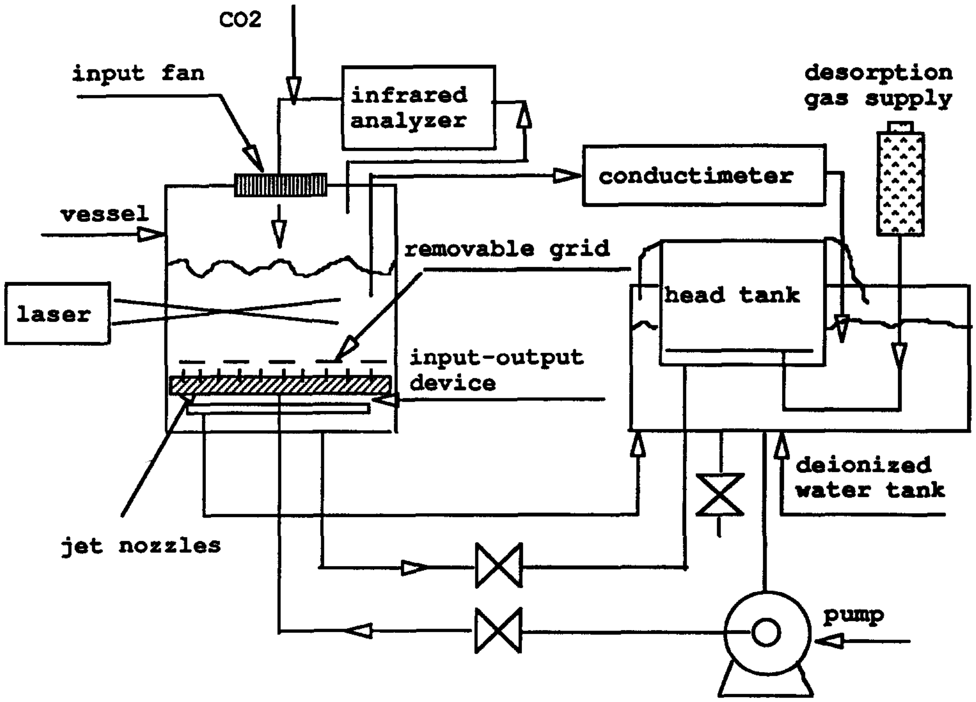

FIG. 1. Experimental facility.

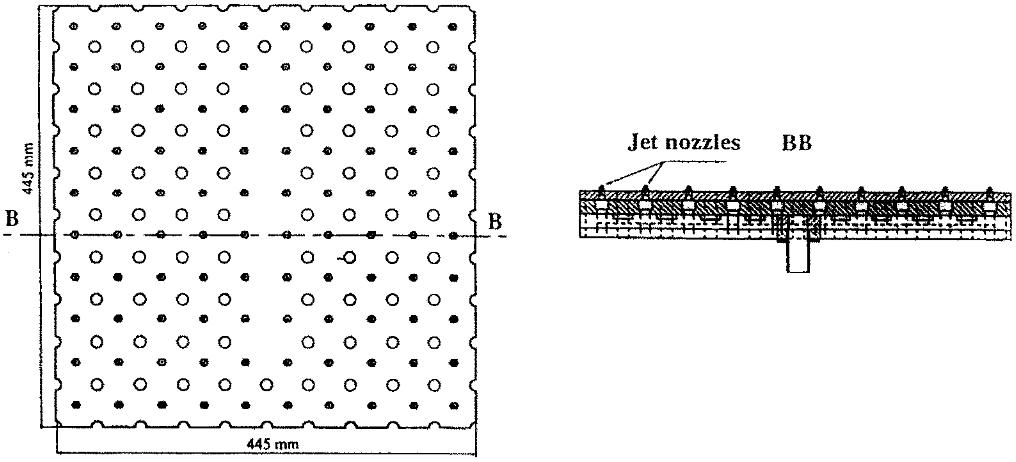

FIG. 2. Input–output device.

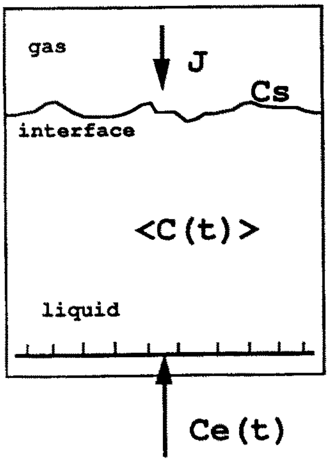

FIG. 3. Absorption scheme.

$$K_L A = q_L \frac{\langle C(t)\rangle - C_e(t)}{C_S - \langle C(t)\rangle}$$

where A represents the interfacial area, $C_e(t)$ the gas concentration at the inlet and q_L the liquid flow rate.

Experimental results and discussion

Dynamical experiments were carried out in the absence of surfactant for the conditions recalled in Table 1. When a surfactant was used (Hexadecanol), experiments were performed for the same dynamical conditions. Films of surface active agent, consisted of 1–6 monomolecular layers of Hexadecanol.

Table 1. Dynamic experimental conditions

Run	q_L (l s^{-1})	h (cm)	u_{MIN} (m s^{-1})
1	0.46	18	0.0533
2	0.46	30	0.0206
3	0.46	39	0.0188
4	0.38	39	0.0159
5	0.35	39	0.0171

The area occupied by a molecule of Hexadecanol was estimated to be $Am = 20 \times 10^{-20}\text{m}^2$ (Sada and Himmelblau [15]). Therefore, a mass equivalent to the desired number of Hexadecanol layers was spread out all over the surface, after being diluted in ether.

As is shown in Fig. 4, the surface tension is reduced when the number of Hexadecanol layers is increased; this result is in good agreement with the values found by Springer and Pigford [16].

After Hexadecanol was used, the liquid surface was carefully cleaned and, before each run, the water was recirculated into the deionizer supply so that interfacial movements could occur freely. The vessel is covered permanently with a Plexiglas lid specially designed to let in the CO_2 and fresh air mixture and to prevent any surface contamination.

Gas absorption results were obtained as described in Table 2, both with and without surfactant. Mass transfer rates obtained in the absence of surfactant are shown in Table 2 while K_L values obtained with a film of surfactant are plotted in Fig. 10.

Experiments without Hexadecanol. Let us first consider experiments carried out without surfactant.

As was shown by Grisenti and George [8], turbulence inside the liquid phase can be approximated as isotropic and the results follow the law predicted by Hopfinger and Toly [17] for a relative distance

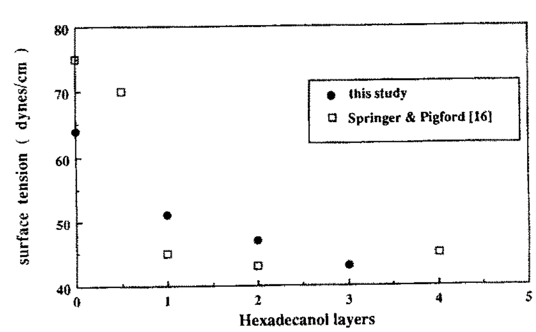

FIG. 4. Surface tension vs number of Hexadecanol layers.

Table 2. Gas absorption experimental conditions with and without surfactant

Run	q_L (l s^{-1})	h (cm)	$10^4 \times k_I$ (m^2 s^{-2})	$10^5 \times K_L$ (m s^{-1}) without surfactant
A	0.46	30.0	6.76	2.72
B	0.46	18.0	23.00	4.93
C	0.46	16.5	60.00	10.40
D	0.46	15.5	110.00	13.00
E	0.46	14.2	150.00	12.90
F	0.46	13.0	190.40	18.50

from the injection plane ($0.45 < z/h < 0.95$). Here, the decay law writes:

$$\sqrt{(\bar{u}'^2)}\ (\text{or}\ \sqrt{(\bar{w}'^2)}) = 1.2\,(z/h-0.3)^{-1}. \qquad (5)$$

However, in the upper region ($z/h > 0.95$), simultaneously with the classical damping of vertical velocity fluctuations, an important increase in the horizontal velocity fluctuations was observed (Fig. 5). The agitation being developed mainly in the horizontal plane is due to the amplification effect on horizontal velocity fluctuations caused by the splatting effect (Hunt [18]), and thus eddies close to the interface are approximately two-dimensional.

In order to understand better the behaviour of these two-dimensional structures, a spectral analysis was carried out while a comparison with the results obtained by Brumley and Jirka [19] was performed.

The increase in the horizontal RMS value close to the surface corresponds with the trend, observed in Fig. 6 for the spectral density of the horizontal velocity fluctuations, where higher values are obtained for lower frequencies. It seems to indicate that large almost two-dimensional eddies develop in the immediate vicinity of the interface. As higher spectral densities are observed for lower frequencies in the horizontal direction, these eddies could behave more like intermittent structures than like classical turbulent eddies.

When velocity fluctuations are plotted, using a normalized RMS horizontal velocity u_N, versus a relative distance to the interface δ_R (Fig. 7), their profiles can be compared with results obtained by Brumley and Jirka [19]. Here $\delta_R = \delta/\delta_S$ is the relative distance to the surface (δ_S is the virtual origin of homogeneous turbulence of which the value, in our experiments, is $\delta_S = 0.7h$ as the distance of the virtual origin to the injection plane is found to be $z_s = 0.3h$) and u_N is defined as the ratio between $\sqrt{(\bar{u}'^2)}$ (or $\sqrt{(\bar{w}'^2)}$) and the minimum value u_{MIN} that $\sqrt{(\bar{u}'^2)}$ takes in the interfacial region. Because the surface-influenced layer is of primary interest, it is convenient to plot the data on the same distorted depth axis as the one adopted by Brumley and Jirka [19], a cube-root distortion is then used.

It can be observed in Figs. 7(a) and (b) that our results are in good agreement with the decay law of Hopfinger and Toly [17] for $\delta_R \geqslant 0.3$. In the intermediate region ($0.1 \leqslant \delta_R \leqslant 0.3$) the influence of the interface is already sensitive and causes a change in the slope of both velocity profiles and leads to the increase observed in the horizontal direction. When the interface is approached, vertical velocity profiles w_N (Fig. 7(b)) decrease and match with the Hunt and Graham [20] profile for $\delta_R \leqslant 0.1$. In the same region, horizontal ones (u_N) fit the law of the non-linear amplification process described by Hunt [18]. No damping in the value of u_N is observed close to the interface except for the case of Run 5. This last case fits the results of Brumley and Jirka [19] and corresponds to McDougall's [21] observations. It can be explained by the following assumption: when the interface is not clean enough or when the agitation level close to the interface is weak (Run 5), experiments are carried out inside what behaves like a viscous wall region and horizontal amplification is no longer observed. However, the increase observed (Runs 1–4) in the value of u_N in that region is much more important than that observed by McDougall [21] or by Brumley and Jirka [19]. Our results are much closer to those described by Thomas and Han-

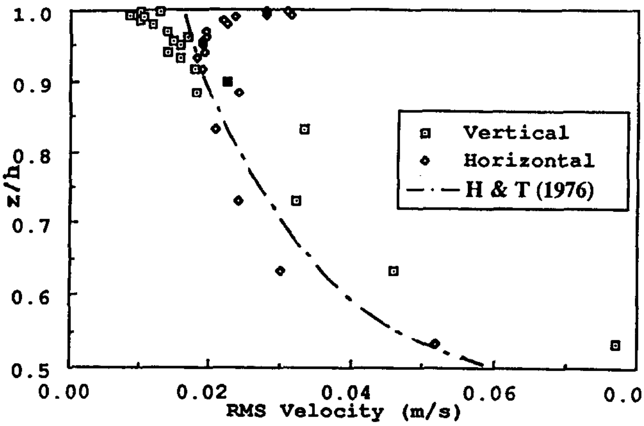

FIG. 5. Horizontal and vertical velocity fluctuations (Run 2). H&T stands for Hopfinger and Toly (Grisenti and George [8]).

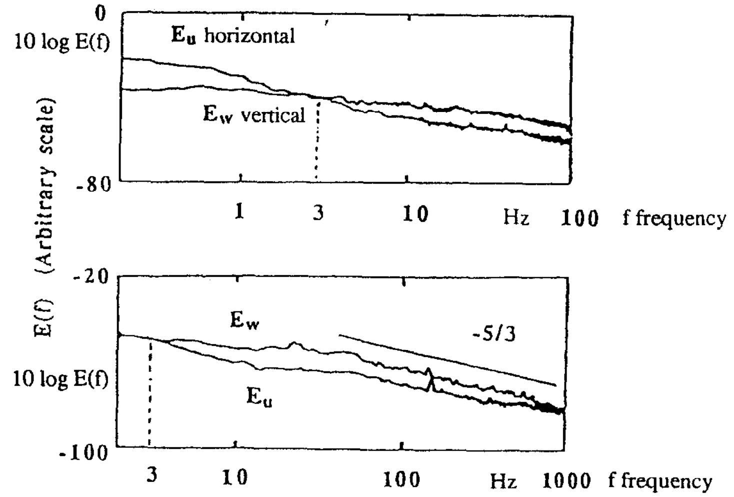

FIG. 6. Horizontal u and vertical w velocity fluctuation power density spectra (Run 2).

cock [22] for a flow over a moving belt in the absence of mean shear stress where a large increase in the RMS value of the longitudinal velocity outside the viscous sublayer was found; however, in their case, there was almost no increase in the RMS value of the spanwise velocity. This could lead to the conclusion that, close to a wall, the enhancement observed in the longitudinal direction is related to the longitudinal mean motion while, close to a free surface, the turbulent agitation is homogeneously redistributed in the horizontal plane as there is no viscous damping at the interface.

Experiments with Hexadecanol. In order to analyze more precisely the interfacial behaviour in the presence of a surface contaminant, it was decided to dispose a film of surfactant at the interface as described above.

Measurements of the RMS horizontal and vertical velocity fluctuations in the horizontal plane 4 mm below the interface are plotted in Fig. 8. Compared to the case of pure water, they show an increase in the RMS vertical velocity value and a relative decrease in the RMS horizontal velocity value for one Hexadecanol layer (Run 2). Here the velocity fluctuations are normalized using the local turbulent kinetic energy value $k_1(\sqrt{(\overline{u'^2})}/\sqrt{k_1}$ in the horizontal plane and $\sqrt{(\overline{w'^2})}/\sqrt{k_1}$ in the vertical direction).

More precisely, when w_N and u_N are defined using the corresponding values of u_{MIN} without surfactant (as it is shown in Figs. 9(a) and (b)), horizontal movements follow the same trend before being damped in the immediate vicinity of the interface. However, this is no longer the case for experiments (Run 1) where, due to the strong agitation remaining close to the surface, the film of surfactant seems to be less efficient and hence the interface behaves more like a clean surface: in such conditions the film of surfactant is probably broken as molecules of Hexadecanol seem to gather into patches spread out at the surface. It can be added that, except in the case of Run 1, horizontal movements reach a higher level than without Hexadecanol before being damped in the immediate vicinity of the interface ($\delta_R \leqslant 4 \times 10^{-3}$). Simultaneously, w_N decreases after a slight increase. Thus, for weaker agitation levels for which this phenomenon is particularly visible, vertical and horizontal movements

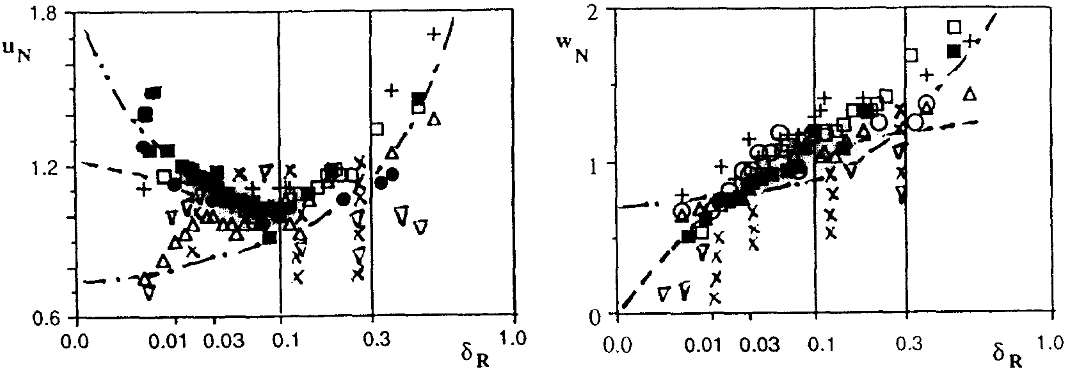

FIG. 7. Normalized velocity ((a) Horizontal, (b) Vertical) vs distance to the interface (after Brumley and Jirka [19]). ——·—— Hunt [18], – – – Hunt and Graham [20], —·— Hopfinger and Toly [17], ∇, x Brumley and Jirka, □, ■, ●, +, △ Present Study (Runs 1–5).

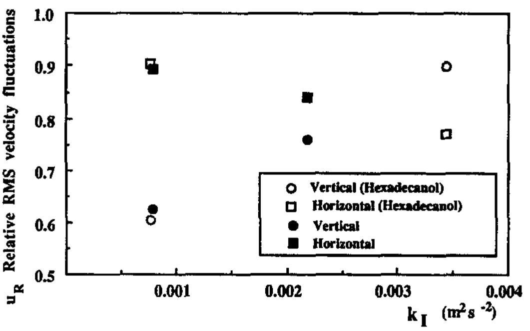

FIG. 8. Relative horizontal and vertical velocity fluctuations (Runs 1 and 2).

are, at first, weakly increased. This is probably due to the diminution of surface tension in the presence of Hexadecanol. On the other hand, very close to the interface a rapid damping of u_N is observed, probably because the cohesion of Hexadecanol molecules at the interface prevents horizontal movements from taking place. It can also be noted that the results obtained by Brumley and Jirka [19] agree rather well with these experiments. As mentioned by these authors, this may be due to the fact that, despite their efforts to keep the interface clean, a slight surface contamination could occur which may prevent horizontal movements from developing freely at the surface and hence the clean surface trends reported above could not be clearly observed in their experiments.

As already shown in Fig. 8, the relative increase in the vertical velocity is in good agreement with the results obtained by Levich [3] and Davies [23] for jets impinging at a free surface, as when surface tension is reduced in the presence of a surfactant vertical agitation can develop more easily. On the other hand, gas absorption experiments show that the conclusions of Levich [3] predicting an increase for K_L proportional to the $(We)^{-1/2}$ are contradicted. K_L results obtained under such conditions are reported in Fig. 10. They show that values obtained in the case of pure water for three temperatures (12, 20 and 27°C) fit relation (3), and that in the presence of Hexadecanol, K_L tends to decrease for the same hydrodynamic conditions. When the number of Hexadecanol layers is increased, it can be added that the interface tends to behave like a solid wall: there K_L values correspond to values predicted by relation (3) where the exponent n takes the $-2/3$ value (corresponding to mass transfer at a solid wall).

The same trend had already been observed in the case of cocurrent gas–liquid flows by Jähne *et al.* [24], or by Caussade *et al.* [9] who carried out simultaneous absorption experiments of CO_2 and Helium and showed that, depending on the wind velocity (that is on the surface agitation level), the Schmidt number power dependency could vary between $-2/3$ and $-1/2$ ($-2/3$ for winds lower than 4 m s^{-1}).

However, if the agitation level is high enough to break the film of surfactant, K_L reaches values even higher than in the case of a clean free surface (for the same hydrodynamic conditions) because the characteristic value $\sqrt{(k_I)}$ can be weakly increased due to the diminution of the average surface tension.

A confirmation of these results would indicate that the relative diminution of the RMS horizontal velocity component, which was also observed by Lee and Luk [25] with bovine serum albumin, is responsible for a behaviour of the interface which varies between that of a solid wall (where $n = -2/3$) and that of a mobile interface (where $n = -1/2$).

In order to verify this trend, CO_2 absorption results presented by Asher and Pankow [12] were analyzed using the Schmidt number power ratio ($Sc^{-2/3}/Sc^{-1/2} = 0.34$ for $Sc = 600$) as a comparison criterion (Fig. 11).

As can be seen, for $(\varepsilon/\nu)^{1/4} > 0.4$, the results roughly gather in two groups depending on the Schmidt number power value, which is in good agreement with our previous remarks concerning the role of a possible surface contamination when one considers that for a given gas n depends only on the interface behaviour. However, the results obtained for a 'lens paper cleaned' interface (Fig. 11) are comparable to results obtained for a film covered interface.

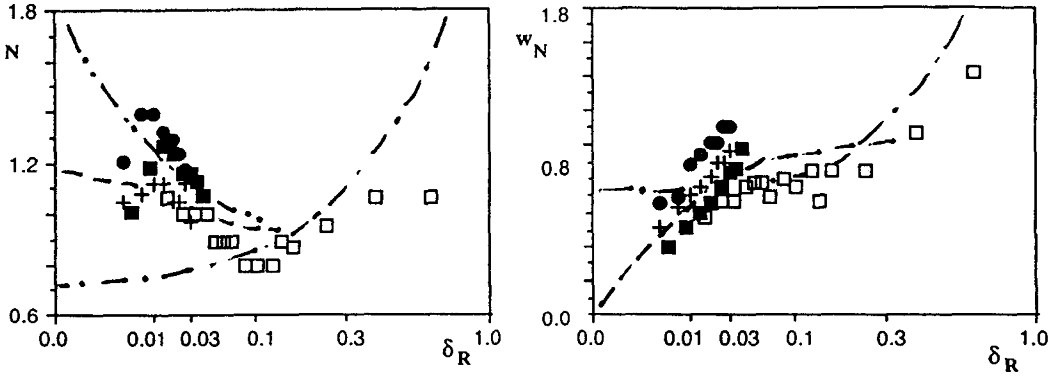

FIG. 9. Normalized velocity ((a) Horizontal, (b) Vertical) vs distance to the interface (after Brumley and Jirka [19]). ——·—— Hunt [18], – – – Hunt and Graham [20], —·— Hopfinger and Toly [17], ∇, x Brumley and Jirka, □, ■, ●, +, △ Present Study (Runs 1 to 5).

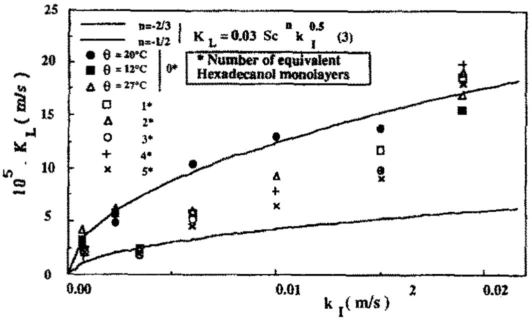

FIG. 10. K_L values with and without Hexadecanol films.

Discussion. One problem, often raised in the literature, concerns the size of the most efficient eddies relative to mass transfer.

Hanratty [7] showed that, gas absorption being controlled by the liquid phase velocity fluctuations normal to the interface in a layer 10–200 microns thick, the characteristic hydrodynamic parameter is the power density spectrum of normal velocity fluctuations in the immediate vicinity of the interface. He showed, from the numerical solution of the unsteady mass balance equation obtained by McCready *et al.* [26] in the case of a wind-sheared interface, that the role of turbulence changes from one in which only low frequency velocity fluctuations are important to one in which the contributions of all frequencies need to be considered.

However, for some authors, large eddies play a dominant role. According to Perkins *et al.* [27] particles are carried to the surface and then back down again, that is the matter released from the interior which reaches the surface in bursts or surface boils (Komori *et al.* [28]), traps matter diffusing from the interface and melts with the inner fluid in downward sweeps (Pankow *et al.* [29]). They find, from their computations and from conceptual models of the Lagrangian integral time scale of the vertical velocities, that these observations are consistent with the fact that large-scale horizontal motions are important. All these considerations agree with results obtained by Chu and Jirka [30] concerning the cocurrent measurements of near turbulence velocity and concentration fluctuations carried out in a stirred vessel. They showed that for rather weak agitation levels the thickness of the gas boundary layer is controlled by large eddies.

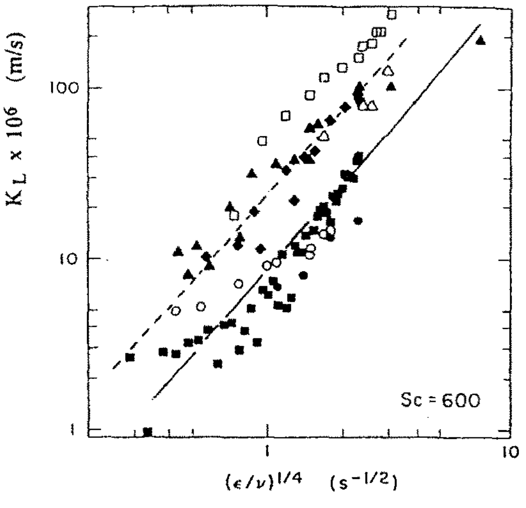

FIG. 11. K_L vs $(\varepsilon/\nu)^{1/4}$ (after Asher and Pankow [12]). – – – $K_L \propto Sc^{-1/2}$, —— $K_L \propto Sc^{-2/3}$, Ratio: $Sc^{-2/3}/Sc^{-1/2} = 0.34$. Clean interface: ◆, ■ Asher and Pankow, □ Broecker *et al.* [37], ▲, △ Jähne *et al.* [24]. Film covered interface: ○ Jähne *et al.* [24]. ● 1-Octadecanol film—Asher and Pankow.

For others, the major role is played by small eddies. For Rashidi and Banerjee [31], for example, there is a high degree of correlation between ejection events of upflowing fluid and the fluid motion near the interface as bursts extend across the water, and for Banerjee [32] the ejection frequency, which coincides with the peak in the wave spectrum for sheared interfaces, gives a characteristic frequency that allows absorption to be calculated using the small eddies concept when in Danckwerts formulation the renewal frequency is equal to the capillary–gravity wave frequency peak, which is in agreement with the model developed by Coantic [33].

For Komori *et al.* [34], who showed recently that organized motions in the air flow intermittently appear on the front of the wave crest and induce surface-renewal motions in the water, K_L is found proportional to the root of this surface-renewal frequency, which corresponds to downward bursts, and increases with increasing the wind shear (but tends to saturate when it reaches approximately 100 Hz).

As was shown by Asher and Pankow [12], K_L is well related to an estimation, due to Cohen [35], of the dissipation rate ε and hence to the smaller eddy scale. It can be added that, as was emphasized by Chu and Jirka [30], for high interfacial agitation conditions there could exist a dual regime with small eddies becoming dominant as proposed by Theophanous *et al.* [36].

From our results, as the power spectra shown in Fig. 6 indicate that the increase in the horizontal velocities is correlated with the development of low frequencies, that is of large two-dimensional eddies, it can be assumed here that low frequency eddies, hence large structures, are primarily responsible for mass transfer. This statement concerning the importance of large eddies is also strengthened by the fact that, when Hexadecanol is added, gas absorption is reduced altogether with horizontal velocity fluctuations.

However, this important question concerning the size of the main structures controlling K_L remains open and its answer will require direct measurements of the dissipation rate ε.

CONCLUSION

Present results show that, in the absence of surfactant, horizontal eddies tend to develop in the immediate vicinity of the interface ($\delta/\delta_s < 0.1$) according to the theory developed by Hunt [20] to account for the non-linear amplification process, and that the slight increase in k_I found in this region corresponds to an increase in the horizontal velocity fluctuations. At a greater distance from the interface ($\delta/\delta_s > 0.3$), the horizontal and vertical RMS velocity profiles follow the decay law predicted by Hopfinger and Toly [17].

The horizontal velocity fluctuation power density spectra also show that horizontal structures are energetic at lower frequencies and could behave more like intermittent structures than like classical turbulent eddies.

When Hexadecanol is added at the surface, K_L tends to decrease. An explanation might be that insoluble surface active agents such as Hexadecanol play two antagonistic roles:

- they enable vertical movements near the interface while surface tension is reduced;
- they reduce the gas interfacial diffusivity and/or they dampen horizontal movements because of the greater cohesion of molecules at the surface.

The explanation linked to the damping of horizontal movements is acknowledged by the fact that, in the presence of surfactant, the Schmidt number dependency of K_L seems to be varying from that of a wall to that of a free surface when agitation levels are increased and hence when surface films are probably broken.

Finally, relation (3) seems to be convenient to predict experimental results:

$$K_L/\sqrt{(k_I)} = 0.03\,Sc^n$$

with n varying between $-2/3$ and $-1/2$ (depending on the agitation level and on the presence or absence of Hexadecanol), and $\sqrt{(k_I)}$ characterizing the interfacial agitation level.

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