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Influence of surfactants on absorption of CO_2 in a stirred tank with and without bubbling

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Abstract

We determined volumetric mass transfer coefficients k_La for the absorption of bubbled and unbubbled CO_2 in a stirred tank, with and without surfactants in the absorbent liquid. In the absence of surfactants, results obtained under continuous liquid flow regimes agreed closely with batch results; accordingly, for convenience, subsequent experiments with surfactant additives were performed only with continuous liquid flow. The results of experiments to determine the dependence of k_La on stirring rate and the kind of bubbling device were fitted to within a 4% error by expressions of the form

$$k_La = K(P_e/V)^{0.4}$$

where P_e is the effective power supplied to the tank, V is the volume of liquid in the tank and K depends on surfactant concentration and the bubbling device and increases linearly with the liquid flow rate. Surfactant reduced k_La by an amount that, to within a 3% error, was proportional to both the corresponding value of k_La in the absence of surfactant and the surface concentration of surfactant. © 1997 Elsevier Science S.A.

Keywords: Surfactant; Absorbtion of carbon dioxide; Mass transfer coefficient

1. Introduction

Determination of the mass transfer coefficients governing the absorption of gases by liquids in stirred tanks is of growing interest because of the common use of these vessels for biotechnological processes whose rates are often limited by the rate of absorption of oxygen. Frequently, it is found that experimental mass transfer coefficients k_L are overestimated by theoretical predictions, a discrepancy usually attributed to the presence of surfactants that have been added to the absorbent liquid to suppress interfacial waves and so facilitate calculation of interfacial area and interpretation of the measured absorption values [1,2]. For absorption through a flat surface, the reduction of k_L by surfactant, whether due to hydrodynamic or barrier effects [3,4], can be offset by stirring [5], which renews the surface; but there are few quantitative data on the influence of surface tension on the volumetric mass transfer coefficient k_La when the gas to be absorbed is bubbled through the liquid phase. Since the presence of surfactants undoubtedly affects the formation and coalescence of bubbles, and hence the interfacial area, it is possible that surfactant-induced reduction of k_L due to barrier effects may be offset by increased area to afford increased values of k_La [6,7].

This article reports the results of experiments on the absorption of bubbled and unbubbled pure CO_2 by water (under continuous flow and batch regimes) or by aqueous sodium lauryl sulphate solutions (under continuous flow regimes) in a stirred tank. Under batch conditions, the influence of stirring rate, stirrer type (paddle or turbine) and bubble plate pore size were investigated; and under continuous flow, the influence of liquid flow rate was studied as well as that of surface tension. To evaluate the payoff between absorption efficiency and power consumption, the volumetric mass transfer coefficients calculated from the experimental data were correlated with the effective power supplied to the system, which was calculated as described below [7].

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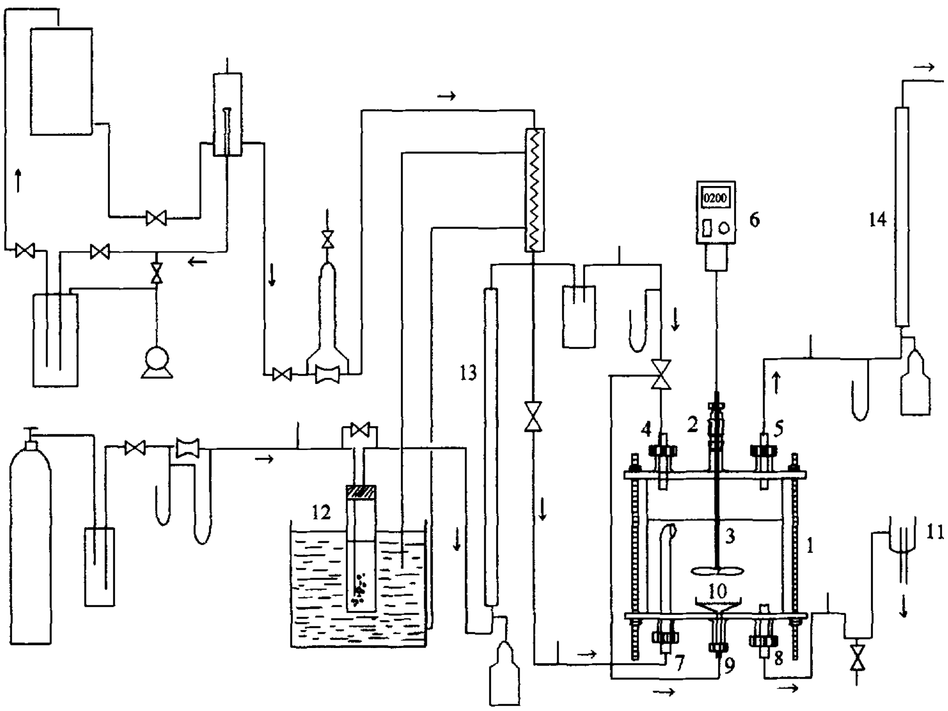

Fig. 1. Experimental set-up for measuring absorption of gas by liquid in a stirred tank with or without bubbling.

Table 1
Equivalent pore size ranges of the bubbling plates used

Plate	Equivalent pore diameter × 10^6 (m)
0	150–200
1	90–150
2	40–90

2. Materials and methods

2.1. Mass transfer measurements

Mass transfer measurements were carried out using the apparatus shown in Fig. 1. Except for the contact device, this set-up has been described in detail elsewhere [8]. The stirred tank used as contact device in this work, 1, was a methacrylate cylinder 14.3 cm in internal diameter and 25 cm high. On its internal wall, four baffles 0.5 cm thick and 1.5 cm wide run from top to bottom in order to prevent vortex formation during stirring. The top plate is flat and has a mercury-sealed central orifice, 2, for the stirrer, 3, and two off-centre orifices for inflow, 4, and outflow, 5, of gas. The stirrer motor used, 6, allowed stirring rate to be varied between 170 and 620 rpm (17.8–64.9 s^{-1}). The baseplate has two off-centre orifices for inflow, 7, and outflow, 8, of the liquid phase, and a central orifice, 9, for inflow of gas through a porous plate 4 cm in diameter, 10, (the pore sizes of the plates used in this work are listed in Table 1). The liquid inflow pipe is so arranged that inflowing liquid enters the bulk liquid in the tank parallel to, and just below, its surface.

The liquid phases used in this work (water and aqueous solutions of sodium lauryl sulphate (SLS) of concentrations up to 5×10^{-3} mass%) were thermostated to room temperature (25 °C) before entering the contact device. For batch runs the liquid load was 2 l. In continuous flow experiments, constant liquid flow rates of between 8 and 18 l h^{-1} were used. The liquid outflow was passed through a tank, 11, whose height was adjusted so that the level of the liquid in the contact device was the same for all flow rates.

The gas to be absorbed, pure CO_2, was passed through a humidifier at 25 °C, 12, and entered the contact device (through either the top-plate inflow port or the porous bubbling plate) at a constant flow rate measured with a bubble flowmeter, 13. Gas outflow through the top-plate outflow port was measured with another bubble flowmeter, 14, before its release into the atmosphere. The gas absorption rate was calculated as the difference between inflow and outflow rates.

2.2. Physical properties

Interpretation of the mass transfer data obtained as described above required knowledge of the densities, viscosities and surface tensions of the liquid phases used, and the diffusivities and solubilities of the gas in these phases. The densities of the surfactant solutions were measured at 25 °C by a pycnometric method, and their viscosities at 25 °C were measured with a Hoppler ball viscosimeter. However, neither of these variables differed significantly from the values for pure water, $\rho = 997$ kg m^{-3} and $\mu = 8.96 \times 10^{-4}$ Pa s [9]. Accordingly, these values were used for all the liquid phases, and the diffusivities and solubilities of CO_2 were also assumed equal to their values for pure water: diffusivity was calculated from the Wilke–Chang equation [10] as

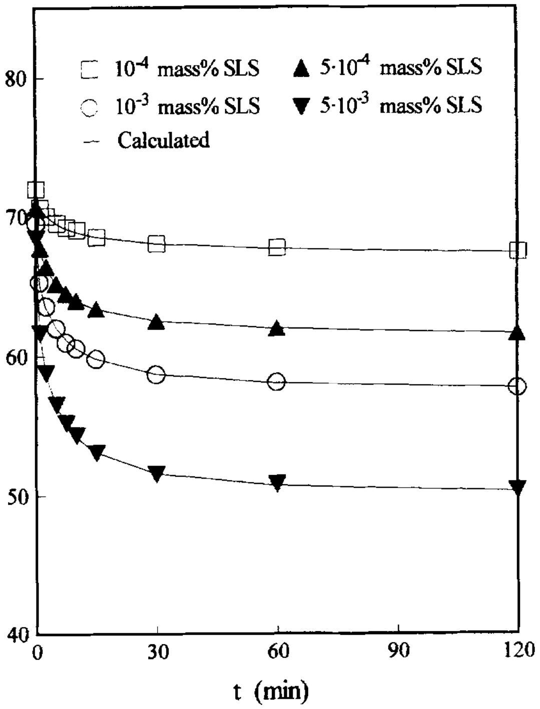

Fig. 2. Time-dependence of the surface tension of aqueous solutions of sodium lauryl sulphate (SLS).

Table 2
Values of the parameter b of Eq. (1)

SLS concentration (mass%)	b ($\mathrm{min}^{-1/2}$)
10^{-4}	0.390
5×10^{-4}	0.432
10^{-3}	0.472
5×10^{-3}	0.516

$1.92\times10^{-9}\ \mathrm{m^2\,s^{-1}}$, and solubility from the equation proposed by Danckwerts–Sharma [11] as $3.36\times10^{-2}\ \mathrm{mol\,l^{-1}}$.

The surface tensions σ of the surfactant solutions used were measured by means a Prolabo tensiometer, which uses the Wilhelmy plate method. The surface tension of fresh solutions varied in time until levelling off after some 2 h; on the basis of published work by Hansen [12] and Nakurama [13], this time dependence was modelled (to within an error of 4%) by the equation

$$\frac{\sigma-\sigma_e}{\sigma_o-\sigma_e}=\exp(-bt^{1/2}) \tag{1}$$

where σ_0 and σ_e are respectively the initial and equilibrium surface tension values and b depends on the concentration of the surfactant. The values of b afforded by fitting Eq. (1) to our data (Fig. 2) are listed in Table 2.

2.3. Calculation of surface surfactant concentrations

The surface concentration of surfactant in the surfactant solutions used was calculated from the measured surface tensions using Frumkin's equation [14]

$$\sigma-\sigma_o=RT\Gamma^\infty\ln(1-\Gamma/\Gamma^\infty) \tag{2}$$

the parameter Γ^∞ having been obtained from Szyszkowski correlations [14] between surface tension at equilibrium and bulk surfactant concentration C_b:

$$\sigma_o-\sigma_e=RT\Gamma^\infty\ln(1+C_b/B) \tag{3}$$

2.4. Calculation of effective power

In the absence of bubbled gas, the effective power supplied to a stirred tank via the stirrer, P_{mo}, is given by

$$P_{mo}=f\bar{\omega}^3d^5\rho_L \tag{4}$$

where ω is the stirring rate, d is the diameter of the stirrer, ρ_L is the density of the stirred liquid and f is a graphically obtained factor that depends on the kind and characteristic length of the stirrer. If the Reynolds number calculated from the characteristic length of the stirrer exceeds 1000, f is practically constant, with approximate values of 1.2 for a paddle stirrer [15] and 1.8 for a turbine stirrer [16]. If gas is bubbled through the stirred tank at a flow rate Q_g, the power P_m supplied to the liquid phase via the stirrer is given by [17]:

$$P_m=0.706\left(\frac{P_{mo}^2\bar{\omega}d^3}{Q_g^{0.56}}\right)^{0.45} \tag{5}$$

The total effective power supplied to the liquid phase, P_e, is now the sum of terms for the stirrer and the bubbling gas [18]:

$$P_e=P_m+C_1P_g \tag{6}$$

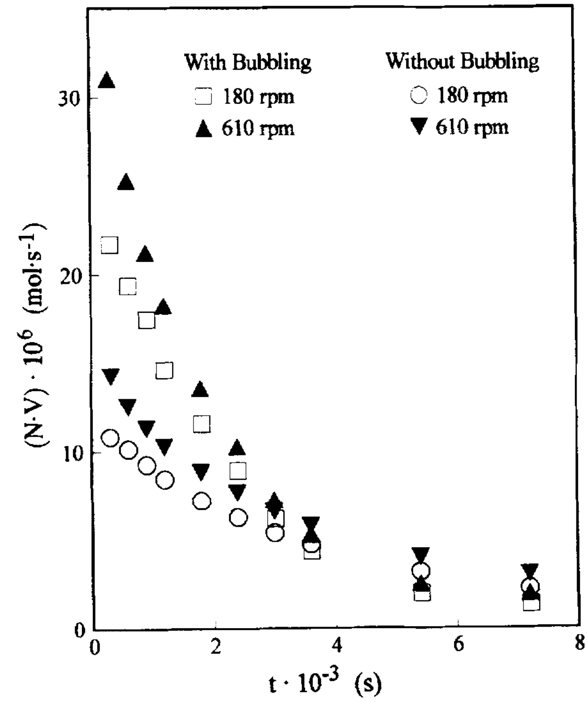

Fig. 3. Time-dependence of the absorption of bubbled and unbubbled CO_2 by water stirred by a paddle stirrer at 180 or 610 rpm, under batch processing conditions.

where the factor C_1 is unity under the operating conditions of this work [19], and P_g, the power supplied by the bubbling gas, is given by a sum of terms for the kinetic energy of the gas and the pressure gradient between the liquid surface and the bubbling plate [20]; specifically,

$$P_g = Q_g \rho_g \left[\frac{\eta u_0^2}{2} + \left(\frac{RT}{M}\right)\ln\left(\frac{\pi_0}{\pi}\right)\right] \tag{7}$$

where ρ_g is density of gas, u_0 is superficial rate, the factor η is unity under the operating conditions of this work [19], M is atomic weight and π and π_0 are the pressures at the liquid surface and the bubbling plate respectively.

3. Results and discussion

N, the amount of gas absorbed per unit time per unit of liquid phase volume, is given by

$$N = k_L a(C^* - C) \tag{8}$$

where C^* is the interfacial concentration of gas at equilibrium (i.e. the solubility of the gas in the liquid phase) and C, the concentration of gas in the bulk liquid, is calculated from the experimental absorption rate data and the liquid flow rate. N is constant under steady state conditions, but under batch conditions must be replaced in Eq. (8) by $\mathrm{d}C/\mathrm{d}t$:

$$\frac{\mathrm{d}C}{\mathrm{d}t} = k_L a(C^* - C) \tag{9}$$

Under all the conditions used in this work, C may be assumed uniform throughout the liquid phase at any given time because of the continuous stirring and the low viscosity of this phase [21].

3.1. Batch processing

In experiments with water as absorbent under batch processing conditions, absorption rate NV (where V is the volume of liquid in the tank) decreased in time and increased with stirring rate. Both these trends were more pronounced for bubbled than for unbubbled gas. Fig. 3 illustrates these results for the paddle stirrer and stirring rates of 180 and 610 rpm.

Integrating Eq. (9) affords

$$\ln\left(\frac{C^*}{C^* - C}\right) = k_L a t \tag{10}$$

and plots of $\ln[C^*/(C^* - C)]$ against time t were fitted well by straight lines through the origin, showing that $k_L a$ was independent of time under the conditions of this work. As Fig. 4 shows, the $k_L a$ data were fitted well by expressions of the form

$$k_L a = K(P_e/V)^{0.4} \tag{11}$$

where P_e is the effective power supplied to the liquid phase (calculated as described in Section 2) and K depended on the bubbling device. Note in particular that although P_e is greater for turbine stirrers than for paddle stirrers operated at the same stirring rate, the ratio between $k_L a$ and $(P_e/V)^{0.4}$ was effectively the same for both kinds of stirrer.

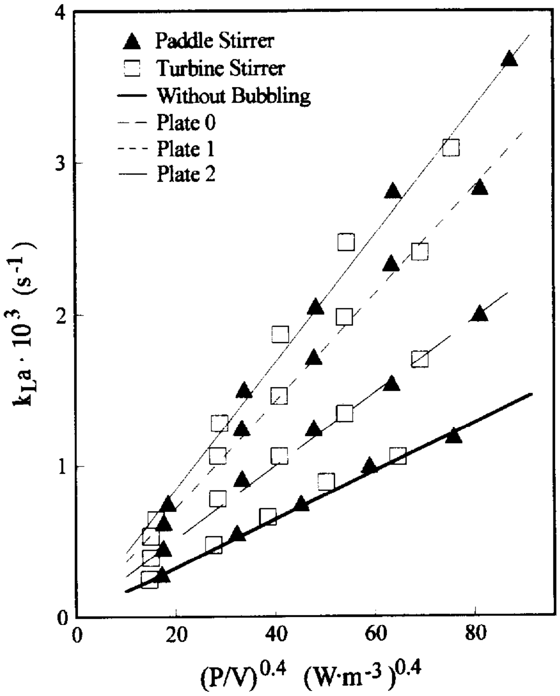

Fig. 4. Dependence of the volumetric mass transfer coefficient $k_L a$ on stirring power for absorption of bubbled and unbubbled CO_2 by water stirred by paddle and turbine stirrers under batch processing conditions.

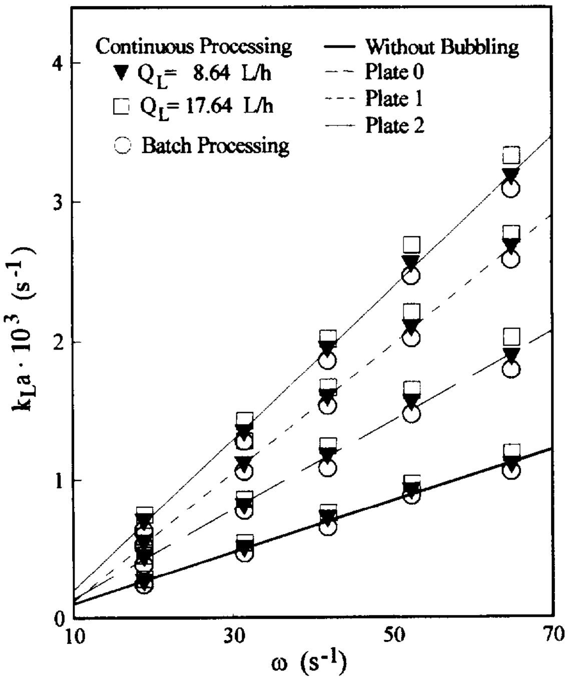

Fig. 5. Dependence of the volumetric mass transfer coefficient $k_L a$ on stirring rate for absorption of bubbled and unbubbled CO_2 by water stirred by a paddle stirrer under batch processing conditions and under continuous processing with liquid flow rates of 8.64 and 17.64 l h^{-1}.

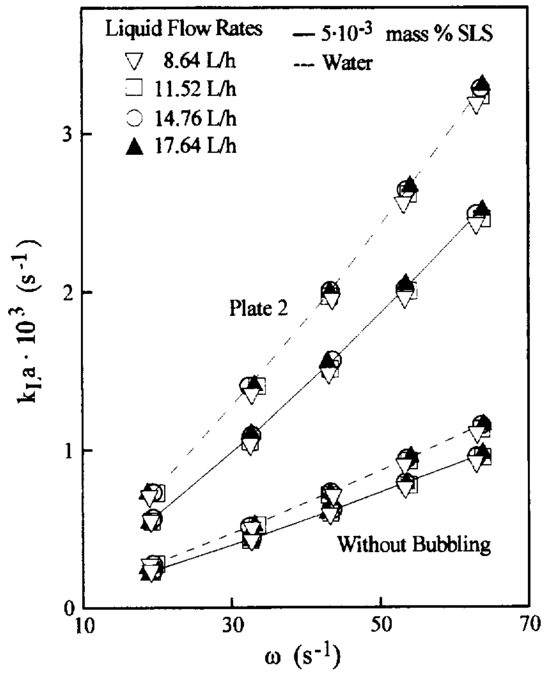

Fig. 6. Dependence of the volumetric mass transfer coefficient k_La on stirring rate for absorption of bubbled and unbubbled CO_2 by water and by 5×10^{-3}% sodium lauryl sulphate stirred by a paddle stirrer under continuous processing at several different liquid flow rates.

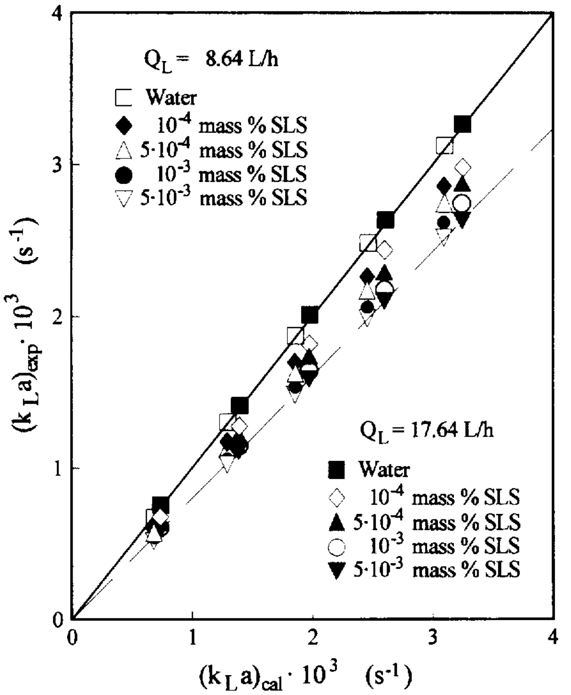

Fig. 7. Experimental values of the volumetric mass transfer coefficient k_La plotted against the values calculated (from Eqs. (11) and (12)) for systems differing only in having pure water as the absorbent.

3.2. Continuous processing

With water flowing at 8.64 or 17.64 l h^{-1} as absorbent, the dependence of k_La on stirring rate and bubbling device was nearly the same as for batch processing (Fig. 5). In view of this, for convenience, only continuous flow regimes were used for experiments with surfactant solutions as absorbent.

Regardless of the presence or absence of surfactant in the absorbent liquid, and regardless of whether the gas was bubbled or not, the values of k_La obtained for a given stirring rate with continuous liquid flow increased easily with liquid flow rate, though the differences between the k_La values for the slowest and fastest flow rates were never more than 8% (Fig. 6). In view of the geometry of the liquid inflow pipe of stirred tank used, this effect may be attributed to the influence of liquid flow rate on surface turbulence.

Since the influence of liquid flow rate on P_e was negligible in comparison with those of the stirring rates and bubbling regime, the Q_L dependence of k_La meant that Eq. (11) could only be fitted well to the experimental data by letting K depend on liquid flow rate as well as on the bubbling device and the surfactant concentration. Specifically, good fit of Eq. (11) (to within a 4% error) was obtained if K was treated as increasing linearly with the liquid flow rate:

$$K=K_0+K_1Q_L \tag{12}$$

with the empirically determined values of K_0 and K_1 listed in Table 3. The values of both K_0 and K_1 decreased with increasing surfactant concentration (the effect on k_La is shown in Fig. 7) and with increasing bubble-plate pore size, (see Table 3; the K_0 values in this table are the K values obtained under batch conditions, which agreed well with the values of

Table 3
Values of the constants K_0 ($m^{1/2}$ $W^{-0.4}$ s) and K_1 ($W^{-0.4}$ $m^{-1.8}$) in Eq. (12)

Plate		SLS concentration (mass%)				
		0	10^{-4}	5×10^{-4}	10^{-3}	5×10^{-3}
Without plate	$K_0\times10^5$	1.580	1.476	1.427	1.395	1.355
	K_1	0.691	0.632	0.611	0.592	0.578
Plate 0	$K_0\times10^5$	2.510	2.346	2.279	2.180	2.105
	K_1	1.017	0.936	0.897	0.875	0.846
Plate 1	$K_0\times10^5$	3.490	3.180	3.112	2.918	2.759
	K_1	1.240	1.096	1.083	1.015	0.959
Plate 2	$K_0\times10^5$	4.180	3.753	3.602	3.409	3.251
	K_1	1.531	1.362	1.307	1.237	1.180

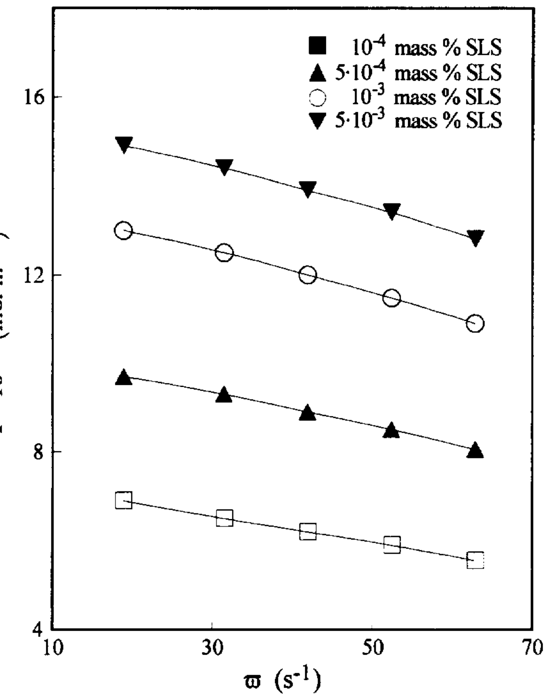

Fig. 8. Dependence of surface surfactant concentration Γ on stirring rate, for paddle-stirred sodium lauryl sulphate solutions.

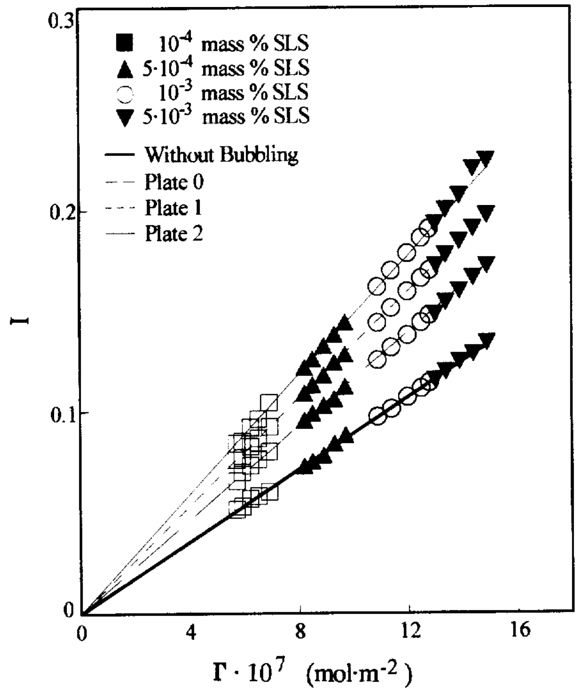

Fig. 9. Dependence of the factor I, Eq. (15), on surfactant concentration Γ.

K_0 obtained by fitting Eq. (12) to the continuous processing results.

The reduction of k_La by surfactant was quantified by a factor I defined by the equation

$$k_La = (k_La)_w - I(k_La)_w \tag{13}$$

where a subscript w indicates a value for the equivalent system without surfactant. Since $I = 1 - k_La/(k_La)_w$, and in view of Eq. (11), I is largely determined by the ratio

$$\frac{K}{K_w} = \frac{K_0 + K_1Q_L}{K_{0w} + K_{1w}Q_L} \tag{14}$$

which, according to the values listed in Table 3, is approximately equal to K_1/K_{1w} for the liquid flow rates used in this work. Hence I is independent of liquid flow rate but does depend on the bubbling device, which affects the interfacial area: for a fixed surfactant concentration, increasing interfacial area by decreasing plate pore size increases I.

Table 4
Values of the parameter K_i in Eq. (15)

Plate	$K_i \times 10^{-5}$ (m^2 mol^{-1})
Without plate	0.89
Plate 0	1.16
Plate 1	1.33
Plate 2	1.48

Surface tension of surfactant solutions were measured for different stirring rate, and under these dynamic conditions the surface tension approximates to the one of non-surfactant system and it remains practically constant while stirring is maintained. Fig. 8 shows the influence of stirring rate on the surface concentration of surfactant, calculated as described in Material and Methods. For a given bubbling device, the factor I was proportional to surface surfactant concentration Γ to within an error of 3% (Fig. 9):

$$I = K_i\Gamma \tag{15}$$

The value of K_i for each bubbling device is listed in Table 4.

4. Notation

a	Interfacial area, m^2 m^{-3}
b	Parameter in Eq. (1), min$^{-1/2}$
B	Parameter in Eq. (3), mol l^{-1}
C	Concentration of gas in the bulk liquid, mol l^{-1}
C^*	Interfacial concentration of gas at equilibrium, mol l^{-1}
C_b	Bulk surfactant concentration, mol l^{-1}
d	Stirrer diameter, m
I	Inhibition factor
k_L	Mass transfer coefficient in the liquid phase, m s^{-1}
K_i	Parameter in Eq. (15), m^3 mol^{-1}
K_0	Parameter in Eq. (12), m$^{-1/2}$ W$^{-0.4}$ s
K_1	Parameter in Eq. (12), W$^{-0.4}$ m$^{-1.8}$
n	Absorption flux, mol s^{-1}
N	Absorption flux per volume, mol l^{-1} s
P	Power, W
Q	Flow rate, m^3 s^{-1}
V	Volume of liquid, m^3

Greek symbols

Γ	Surface concentration of surfactant, mol m^{-2}
Γ^{∞}	Parameter in Eq. (2), mol m^{-2}
μ	Viscosity, kg m^{-1} s
ρ	Density, kg m^{-3}
σ	Surface tension, mN m^{-1}
ω	Stirring rate, s^{-1}

Subscripts

g	Gas
L	Liquid
e	Effective
m	Mechanical
o	Without bubbling

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