

## MASS TRANSFER RATE FROM GAS BUBBLES INTO LIQUID IN PRESENCE OF SOLID PARTICLES WITH STRONG ADSORBING PROPERTIES

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*Dedicated to late Academician Eduard Hála.*

The presence of small particles with adsorbing activity (carbon soot, active carbon etc.) in the bubble bed augments the gas-liquid mass transfer coefficient  $k_L a$  about approximately 20% in comparison with pure liquid. This fact can be explained by penetrating and disturbance effect of particles into the boundary layer of liquid near the interface. This activity is however reduced to small concentrations of particles (0.07% mass in the case of carbon soot, 0.5–1.0% mass for active carbon particles). Addition of small amount of particles with adsorbing activity to the liquids containing superficial active agents (tensides) can partially overcome the negative effect of tensides on  $k_L a$  value. The positive effect of particles of active carbon on  $k_L a$  in bubble beds is less pronounced than that published for the case of mechanically agitated vessels.

It has been commonly accepted that the presence of solid particles in bubble beds could significantly influence the interfacial mass transfer between gas bubbles and the liquid phase. We summarized the probable effect of the solid particles on the value of volumetric mass transfer coefficient  $k_L a$  in the following table.

Unfortunately, more quantitative information which would permit reasonable mass transfer prediction is not available. One of the scarce resources<sup>1,2</sup> is our equation for gas porosity of bubble bed in the presence of solid glass spheres of diameter 36–280  $\mu\text{m}$  for the turbulent regime of bubbling (heterogeneous suspension)

$$\varepsilon_G = w_G / (P + 2w_G) \quad (1)$$

$$P = 0.29 + 0.031c_s^{0.45}, \quad c_s \text{ in mass } \%, (0-10\%) \quad (2)$$

which permits mass transfer coefficient estimation according to our correlation

$$k_L a = 0.83Kw_G^{0.65}\varepsilon_G^{0.35}(1 - \varepsilon_G)^{0.65}, \quad w_G \text{ in cm/s.} \quad (3)$$

Parameter  $K$  in the Eq. (3) has to be evaluated for the respective pure liquid experi-

mentally ( $K(\text{H}_2\text{O}) \doteq 0.05$ , for  $w_G$  in cm/s). In contrast to the paper of Joosten<sup>3</sup> any positive effect of the presence of solid particles on  $k_L a$  in heterogeneous suspensions was observed  $d_s = 24-280 \mu\text{m}$ ,  $c_s = 2.5-10\%$  mass in our experiments<sup>1</sup>. The decreasing  $k_L a$  in heterogeneous suspension corresponds with decreasing gas hold-up. Generally we have to accept the fact that mass transfer coefficient  $k_L a$  in the heterogeneous suspensions is negatively affected when compared with pure liquids.

In the case of homogeneous suspensions we have studied earlier<sup>1</sup> mass transfer coefficient dependence for the suspension of inert particles, without superficial adsorbing activity (ZnO suspensions). Apparently, the presence of such type of particles acts on the value of  $k_L a$  very harmfully. We judge on blocking of effective interfacial area (for the concentration up to 2.5 mass m) as the porosity remains in that concentration region almost constant. The bubble coalescence is promoted by the increased concentration of ZnO particles, with consequent decrease of gas hold up and hence also decrease of  $k_L a$ . General correlation of the mass transfer coefficient  $k_L a$  for homogeneous suspension is not available. However, our experimental results previously published<sup>1</sup> can be used as a first approximation for  $\varepsilon_G$  and  $k_L a$  prediction.

As a base for mass transfer coefficient prediction one must know the gas phase porosity  $\varepsilon_G$  in the respective homogeneous suspension. The general formula for an approximative  $k_L a$  value estimation can be used:

$$k_L a = K^* w_G^{0.65} \varepsilon_G^{0.35} (1 - \varepsilon_G)^{0.65}, \quad (4)$$

parameter  $K^*$  in Eq. (4) must be evaluated experimentally. For suspensions of inert particles in water we propose the formula

$$K^* = 0.04/\exp(0.07c_s), \quad (5)$$

$c_s$  in mass m,  $w_G$  in cm/s.

Unfortunately, there are very scarce data for homogeneous suspensions of particles with strong adsorbing properties. It is likely that the porosity of such suspensions will not be very different as compared with homogeneous suspensions of inert particles. However, if that particles are sufficiently small it may affect the value of  $k_L a$ . There is some evidence in the literature about positive effect on  $k_L a$ , mainly for active carbon particles in the agitated catalytic slurry reactors<sup>4</sup>. No correspondent information for bubble bed reactors is at present available. On the other hand, the reaction rate of the majority of multiphase gas-liquid chemical and biochemical industrial processes depends on mass transfer. The effort should be therefore made to increase, in the energetically plausible way, the intensity of mass transfer in the reactor, namely the  $k_L a$  value. The gas phase velocity in the reactor has to be mostly maintained constant in the reactor. According to Table I only two feasible methods how to increase the  $k_L a$  are possible: addition of large particles with the purpose

TABLE I  
Influence of solid particles on the value of mass transfer coefficient  $k_L a$  in the bubble bed on different type of suspension

Size of particles	Action on $k_L a$	Possible mechanism	Note	Ref.
Fluidized bed				
1 000 $\mu\text{m}$	enhancement	collision of bubbles with particles having large inertia can cause break-up of bubbles; $a$ increases	increase of $k_L a$ 20%—100%	5
				6
Heterogeneous suspension				
5—1 000 $\mu\text{m}$	enhancement	small increase of relative viscosity does not influence the bubble coalescence but results in reducing of ascending velocity of bubbles $\hat{=}$ increase gas hold-up	limited to small concentrations only; max. increase of $k_L a$ 10—20%	3
	hindering	pronounced increase of viscosity of suspension and ceasing turbulence in the bed is favourable to promote the rate of coalescence of bubbles	higher conc. of particles	3
Homogeneous suspension				
0—5 $\mu\text{m}$	enhancement	disturbance of the diffusional boundary layer results in $k_L a$ increase. Particles with great adsorption capacity can penetrate through the diffusional film and pick up adsorbate and transfer it to the bulk	limited to small concentrations of particles only	4, 7
	hindering	accumulation of particles on interfacial surface diminishes the magnitude of the effective interfacial area	higher concentration of particles, inert particles	8
	hindering	increasing relative viscosity of suspension results in increasing the rate of coalescence of bubbles	higher concentration of bubbles	

to establish the fluidized bed or, alternatively, addition of small particles with adsorbing activity with the aim to form homogeneous suspension and to increase the mass transfer from bubbles. Limited gas and liquid velocity in the reactor makes often impossible to apply the method of fluidized bed.

It is the aim of this paper to give experimental evidence which could elucidate the role of presence of small particles with adsorbing properties on the mass transfer phenomena in the bubble bed column reactors. In this contribution we have limited ourselves to a homogeneous regime of bubbling only.

## EXPERIMENTAL

### *Apparatus*

The single-stage bubble column, column diameter 0.142 m. Experiments were carried out at zero liquid flow rate. Stainless steel perforated plate, hole diameter  $d_0 = 0.5$  mm, free plate area 0.2%. Clear liquid height 250 mm. Superficial gas velocity was varied between 0.18–1.44 cm/s (100–800 L/h).

### Solid Phases

1. *Carbon soot*. Carbon soot recovered in the form of carbon soot waste water from the industrial technology of hydrogen production via heavy oil gasification was accumulated as a paste with 6% of a dry matter by multiple centrifugation and resuspension in distilled water. Concentration of soot in the column:  $c_s$  mass %: 0, 0.07, 0.157, 0.29, 0.44, 0.7. Size of particles: Leitz-Classimate microscope has been used for the measurement of particle sizes. The accurate determination of size is very difficult. The particles form huge agglomerate on the air-water interface which are in the incessant movement. Old agglomerates desintegrate and new clusters create. Solid clusters formation in the range of sizes 100–200  $\mu\text{m}$  was measured. The individual components of this clusters do not extend beyond the size 7  $\mu\text{m}$ ,

2. *Active carbon*. a) Coarse particles: Commercial product, purified by multiple decantation in distilled water and dried. It is difficult to distinguish among the agglomerate and individual particles. The correspondent solid formations size between 7–2 000  $\mu\text{m}$ . No particles below 7  $\mu\text{m}$  were found. b) Fine particles: Coarse particles of purified and dried carbon were powdered in the ball-mill. The apparent diameter of individual particles varies between 0.4–2.6  $\mu\text{m}$  approximately. The sizes of agglomerations fall in the range 5–10  $\mu\text{m}$ . Both fractions were used as a suspension in water.  $c_s$ , wt. %: 0, 0.14, 0.28, 0.56, 1.12, 2.24, 4.48.

3. *Carbon soot and tenside*. Experiments were carried out with soot-in-water-suspension,  $c_s = 0.07$  mass %, gas flow rate 400 l/h. Tenside (superficial active additive, SAA) was a commercial product TAL (esters of sucrose in water solution containing 35% of active component. Concentration of the tenside: 0.2, 0.4, 1.4, 3.0, 4.6, 6.2 ml in 3.8 liter of liquid. The aim of application of tenside was to disperse the agglomeration of particles of soot in the water and to examine simultaneous effect of tenside and fine particles on mass transfer coefficient.

### Determination of Gas Holdup and $k_L a$

Bubble bed expansion measurement was used for gas holdup determination. The height of aerated bed was determined visually from the position of polystyrene-ring float. The dynamic

method was applied for  $k_L a$  measurement based upon monitoring of the unsteady oxygen absorption into previously deoxygenized water in the bed. The Clark-type fast-response electrode was located in the by-pass tubing out of the bed in the loose vicinity of the column. The liquid from the bubble bed was pumped into the tube and proper velocity of the liquid was maintained close by the membrane to prevent the diffusional resistance.

## RESULTS AND DISCUSSION

### Carbon Soot

$k_L a$  Data are plotted in Fig. 1. As can be seen from the graph, only very small addition of particles is favourable to  $k_L a$  enhancement. Negative effect of solid phase on  $k_L a$  values was observed when increasing the concentration of solid particles above the concentration of 0.157 mass %. The  $k_L a$  value for the concentration  $c_s = 0.157$  mass % is essentially the same as the value of  $k_L a$  in pure water. However, the gas holdup differs (it is lower) in comparison with pure water. We can explain this phenomena with the help of the concept of disturbance of the boundary layer adjacent to the interface by penetrating particles. Above this concentration the influence of particles on increasing the bubble coalescence prevails and the  $k_L a$  value sharply decreases, like in the case of homogeneous suspensions of inert particles.

### Active Carbon

Slight increase in  $k_L a$  can be recorded up to the concentration of 1 mass % approximately. Both carbons (coarse and fine) behave in a similar manner. Above this concentration the  $k_L a$  values fall gently, see Figs 2 and 3. The increase of  $k_L a$  in the domain of small concentration of particles can be explain like in the case of soot. When increasing the active carbon concentration we have measured the gas holdup

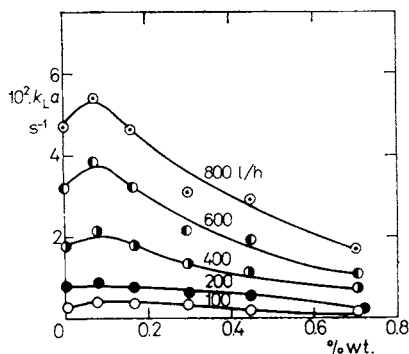


FIG. 1

Dependence of  $k_L a$  on soot concentration

even superior to pure water, see Fig. 4. We can suppose that predominant phenomena here is blocking of effective interfacial area as in the case of inert particles.

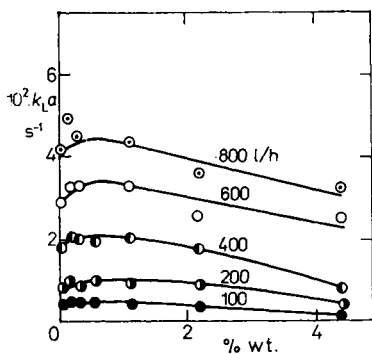


FIG. 2

Dependence of  $k_L a$  on solid phase concentration at various gas flows. Particles of coarse active carbon

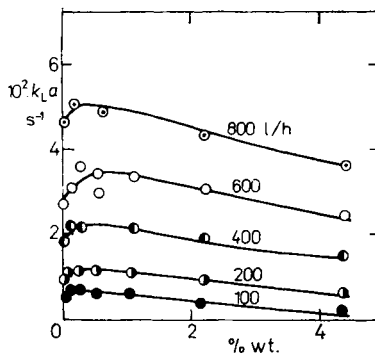


FIG. 3

Dependence of  $k_L a$  on solid phase concentration at various gas flows. Particles of fine powdered active carbon

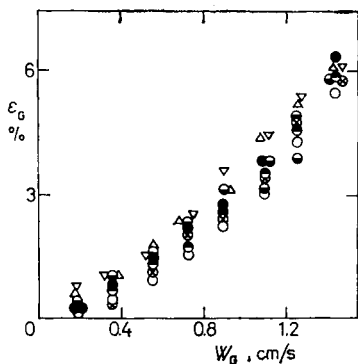


FIG. 4

Dependence of gas holdup on  $w_G$  at various solid phase concentrations  $c_s$ , mass %:  $\circ$  0.07,  $\ominus$  0.14,  $\otimes$  0.28,  $\omin�$  0.56,  $\Delta$  0.24,  $\nabla$  4.48,  $\bullet$   $H_2O$

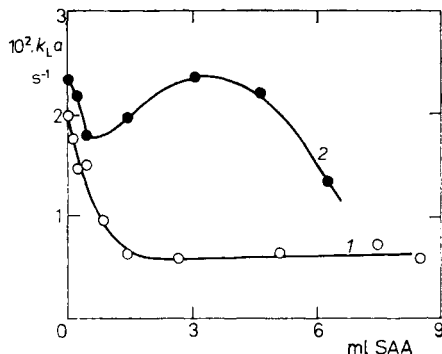


FIG. 5

Dependence of  $k_L a$  on SAA concentration. Reactor volume 3.8 l, height of clear liquid 250 mm, gas flow 400 l/h. 1  $H_2O$ , 2 with 0.07 mass % of soot

*Soot and Tenside*

In many practical applications namely in biochemical reactors we have to count with the presence of superficial active agents (SAA). In our previous work<sup>9</sup> we concluded that the SAA sharply influenced the hydrodynamic conditions in the laminar sublayer of the boundary film and hence hindered the interfacial mass transfer. For various types of tenside additives we have verified a semitheoretical equation for the mass transfer coefficient prediction in the form

$$\frac{1}{\psi^2} = K_2 \left( \frac{\sigma_0 - \sigma}{\psi} \right) + b \left( 1 - \frac{\sigma_0 - \sigma}{\sigma_0} \right), \quad (6)$$

$$\psi = k_{L,SAA}/k_L,$$

where  $k_{L,SAA}$  and  $k_L$  are the mass transfer coefficients in the solution with SAA and in pure solvent respectively,  $\sigma$  are surface tensions of the solution with SAA and of pure solvent respectively.

As a result of our investigation we can consider parameter  $b$  as universal constant,  $b = 1.7$ . Parameter  $K_2$  is a constant, the value of which depends on the group of SAA used. Such individual groups of SAA with similar behaviour at the gas-liquid interface are for example alcohols, sodium salts of fatty acids, Tweens, product of cell metabolism, etc. For each group of SAA it is necessary to determine the value of constant  $K_2$  experimentally.

The appropriate models for the  $K_2$ -constant correlation (if any) should usually contain other constants and liquid-phase physico-chemical parameters.

For alcohols as an example such correlation has the form

$$K_2 = 340/[1 + 52(\sigma_0 - \sigma)], \quad (7)$$

the dimension of  $\sigma$  in N/m.

On the other side, small concentration of solid additives enhances mass transfer and its presence could be useful to overcome the negative hydrodynamic effect of SAA. The result of the simultaneous action of SAA and fine particles with adsorbing activity can be seen in the Fig. 5. Addition of SAA at first evokes the drop in mass transfer coefficient value, which can be explained as a result of hydrodynamic effect of SAA. Next addition of SAA results however in temporary increase of  $k_L a$ .

One of the possible explanations of this fact is that SAA dissolves the agglomeration of fine particles at the interface and helps them to penetrate into the diffusional film. At high concentration of SAA the negative effect of SAA on boundary layer hydrodynamics prevails.

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