EFFECT OF SCALE-UP ON RATE OF INTERFACIAL MASS TRANSFER IN SHALLOW-BED BUBBLE COLUMN REACTORS

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Absorption rates of CO_2 into aqueous solutions of sodium hydroxide were measured in shallow-bed bubble columns with sieve trays as gas distributors. Experiments were carried out in two cylindrical columns (ID 0·15 and 0·30 m) and in a rectangular unit with square cross-section 1 m^2. Liquid side mass transfer coefficients (k_L) and specific interfacial area (a) were evaluated from experimental data of absorption rates. The effect of bubble-bed dimensions on mass transfer characteristics is discussed and recommendations for scale-up of bubble column reacfors are presented.

Our contribution is concerned with the effect of scale-up of dimensions of the bubbled bed on intensity of interfacial mass transfer in bubble-type column reactors with sieve trays used as gas distributors. The aim was to determine the effect of bed height and diameter on quantities characterising the interfacial mass transfer in gas-liquid systems namely on specific interfacial area a and liquid side mass transfer coefficient k_L. The study has been confined to so-called shallow beds, *i.e.* beds characterised by low ratio of clear liquid height to bed diameter H_0/D_K.

It is known that in such beds the character of gas–liquid dispersion changes significantly with the bed height. By visual observations it has been proved that at low clear liquid heights ($H_0/D_K \leq \leq 1$) the character of bubble bed corresponds to the "homogeneous" bubbling regime[1] independently of geometry of the distributing plate, while at the increase of liquid bed height (larger values of ratio H_0/D_K) transition to "turbulent" bubbling occurs when common types of distributing plates are used. Indeed it is thus possible to expect that such changes in the character of the bubbled bed can significantly affect the intensity of interfacial mass transfer in the bed and consequently its characteristic parameters k_L and a. Experimental evidence concerning the effect of bubble-bed dimensions on mass transfer characteristics has therefore a vital importance for design of bubble-type reactors and for their scale-up.

For determination of k_L and a the method of absorption of CO_2 into aqueous solutions of sodium hydroxide has been chosen. This method has been videly used for these purposes and its detail description as well as discussion of its shortcommings can be found *e.g.* in the recent paper by Schumpe and Deckwer[2]. The absorption rates were measured in bubbled bed in three experimental units as function of gas flow rate, column diameter and clear liquid height and values of k_L and a were calculated from experimental data. At derivation of relations for the absorption rate ideal mixing of the liquid phase and plug flow of gas phase have been assumed. Validity of both these assumptions has been proved previously[3,4].

THEORETICAL

Absorption of CO_2 from its mixture with air into aqueous solution of NaOH can be described by equation

$$CO_2 + 2 OH^- \rightarrow H_2O + CO_3^{2-} \tag{A}$$
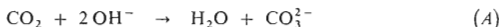
under assumption that

$$c_A < 0.45 c_{B0}, \tag{1}$$

where c_A is the sum of CO_2 and CO_3^{2-} concentrations and c_{B0} is the initial concentration of OH^-. If further conditions are fulfilled

$$\sqrt{M} < E_i/4 \tag{2}$$

$$1 < \sqrt{M} < 4 \tag{3}$$

$(M = D_A k c_B / k_L^2, E_i$ is the enhancement factor) the absorption rate of CO_2 into aqueous solutions of NaOH in a bubble column $(Ra = dc_A/dt)$ can be expressed by relation

$$Ra = \bar{P}_A a / [1/k_G + H_A / \sqrt{(D_A k c_B + k_L^2)}], \tag{4}$$

where $\bar{P}_A$ is the mean partial pressure of CO_2 in gas phase, calculated under assumption of plug model of gas flow through the bed. When the gas-side resistance can be neglected (this assumption has been verified experimentally) equation (4) can be written in a simplified form

$$Ra = a\bar{c}_A^*(D_A k c_B + k_L^2). \tag{5}$$

If condition (1) is fulfilled, concentration c_B in Eq. (6) can be expressed from relation

$$c_B = c_{B0} - 2c_A \tag{6}$$

and Eq. (5) can be re-written into the form

$$dc_A/dt = a\bar{c}_A^* \sqrt{[D_A k(c_{B0} - 2c_A) + k_L^2]}. \tag{7}$$

It is obvious from data published by D'Ans-Lax[5] and Danckwerts[6] that the Henry's law constant H_A and thus also c_A^* change only insignificantly by reaction of NaOH to Na_2CO_3. Similarly it can be assumed that diffusivity D_A remains practically constant as the increase of solution viscosity due to reaction is negligible. It has been

proved that the total relative change of c_A^* and D_A due to reaction (A) does not exceed 2%.

If under these assumptions Eq. (7) is integrated for the initial condition

$$t = 0 \quad c_A = 0 \tag{8}$$

relation is obtained

$$t = \frac{\sqrt{(D_A k c_{B0} + k_L^2)} - \sqrt{[D_A k(c_{B0} - 2c_A) + k_L^2]}}{D_A k \bar{c}_A^* a} \tag{9}$$

and after its re-arrangement final relation for c_A can be obtained in the form

$$c_A = t a \bar{c}_A^* \sqrt{(D_A k c_{B0} + k_L^2)} - t^2 D_A k a^2 (\bar{c}_A^*)^2 / 2 . \tag{10}$$

Experimental data of c_A versus t were fitted by Eq. (10) using a nonlinear regression method[7] and for individual sets of experimental conditions (w_G, H_0, D_K) the corresponding values of k_L and a were obtained.

EXPERIMENTAL

Measuring units. Experiments were performed in two cylindrical glass-wall columns with $D_K = 0.15$ and 0.3 m and in a rectangular unit with side length 1 m. Perforated plates with hole diameters $d_0 = 1.6$ mm and free plate area $\varphi = 0.5\%$ were used in all three units as gas distributors. Plate geometry ensured stable plate performance and uniform gas distribution[1]. Experiments in all three units were performed batchwise at superficial gas velocities $w_G = 0.05$ to 0.20 m/s. Ratio of clear liquid height to characteristic dimension of individual units (D_K, l) ranged between 0.15 and 4. Distilled water was used for experiments in both cylindrical columns, while experiments in the rectangular unit were carried out with tap water. To estimate the possible effect of liquid phase properties on absorption rate data two sets of testing experiments were performed in the column with $D_K = 0.15$ m with both tap and distilled water. No significant differences between k_L and a data from both sets of experiments were observed.

Measuring procedure. In the unit was for fixed clear liquid height H_0 set up the gas flow rate corresponding to the appropriate superficial gas velocity w_G, and mixture of CO_2 with air started to be introduced into the bed in time t_0. Samples of liquid phase were taken (usually 8 samples in one minute intervals) and were analysed by the method developed by Minárik[8] for determination of low CO_2 concentrations.

Reaction rate constant k, Henry's law constant H_A and concentration of CO_2 at the interface c_A^* were calculated from relations presented by Pohorecki and Moniuk[9]

$$\log k = \log k_\infty + 0.1498 I \tag{11}$$

$$\log k_\infty = 11.944 - 2 382/T \tag{12}$$

([k] = m^3/kmol s)

$$\log (1/H_A)_S = \log (1/H_A)_W - I_i h_i \tag{13}$$

$$\log (1/H_A)_W = 6.1229 - 5.9044 \cdot 10^{-2} \, T + 7.8857 \cdot 10^{-5} \, T^2 , \tag{14}$$

where $[H_A] =$ atm cm^3/mol, 1 atm $= 0.1$ MPa

$$c_A^* = P_A / H_A , \tag{15}$$

where P_A is corrected for vapour pressure of water according to

$$P_A = 0.97 V_A / V . \tag{16}$$

Diffusivity D_A was calculated from Eq. (17) presented by Danckwerts[6]

$$(D_A)_S = (D_A)_W / (\mu_{rel}^{0.85}) , \tag{17}$$

where

$$(D_A)_W = -4.1764 + 712.5/T - 2.591 \cdot 10^5/T^2 \tag{18}$$

$$(\mu_{rel}) = 1 + 0.288 c_{B0} \tag{19}$$

$[D_A] =$ cm^2/s, $[c_{B0}] =$ kmol/m^3.

RESULTS AND DISCUSSION

Using the procedure described above, values of specific interfacial area and liquid--side mass transfer coefficient were calculated from Eq. (10). In accordance with theory[10] and with the results reported by Sharma and Mashelkar[11] and by Pasiuk–Broni-kowska[12], values of k_L were for all combinations of D_K and H_0 reasonably constant and independent of the gas flow rate w_G. Average value of k_L calculated from all the experiments considered was $(k_L)_{av} = 2.1 \times 10^{-3}$ m/s. This value is about five times larger than data reported by Danckwerts[6] which are based on the results of Sharma and Mashelkar[11], however they are in a very good agreement with data obtained for the same system by Pasiuk–Bronikowska[12]. To eliminate the effect of fluctuations of k_L on specific interfacial area, the average calculated value $(k_L)_{av} = 2.1 \times 10^{-3}$ m/s was substituted into Eq. (10) for k_L and the experimental data fitting was repeated with a as a single regression parameter. Only these corrected values of a are considered in the following part.

As could be expected, specific interfacial area increased with increasing superficial gas velocity. This case is demonstrated in the form of dependence of a on w_G for columns with $D_K = 0.15$ and 0.30 m in Fig. 1. The non-linear shape of experimental dependence could be well correlated by the exponential function $a \sim w_G^x$ where the average value of exponent $\bar{x} = 0.65$ obtained from our experimental data agrees fairly well with the value 0.7 recommended by Sharma and Mashelkar[11].

The effect of column diameter and clear liquid height on specific interfacial area is clearly demonstrated in Fig. 2, in which data of a obtained at $w_G = 0.05$ m/s are

plotted in dependence on D_K for various values of H_0. Interfacial area decreases with increasing clear liquid height. Keeping other conditions constant interfacial area increases with the increase of column diameter from $D_K = 0.15$ to 0.30 m, while significantly lower values of specific interfacial area were again observed in the rectangular unit ($l = 1$ m).

In Fig. 3 data of specific interfacial area are plotted against the ratio H_0/D_K (for $w_G = 0.05$ m/s). This plot clearly demonstrates identity of dependences of a on H_0/D_K obtained in both cylindrical columns i.e. for $D_K = 0.15$ and 0.30 m. The dependence obtained in the rectangular unit has a similar shape, values of a are however significantly lower for corresponding H_0/D_K values. It can be concluded on basis of the data from both cylindrical columns that in the region of considered column diameters there is always a single value of specific interfacial area corresponding to each value of ratio H_0/D_K (at constant w_G), independently on specific values of D_K and H_0. It is the value of ratio H_0/D_K which should be used for characterisation of the effect of bubble bed dimensions on mass transfer characteristics instead of the separate values of H_0 and D_K. Similarly it has to be recommended that the H_0/D_K ratio should be kept constant at scale-up of bubble column dimensions. In Fig. 4 average values of specific interfacial area obtained in columns with $D_K = 0.15$ and 0.30 m are plotted agains H_0/D_K for various gas flow rates. The dependences have been succesfully correlated by the exponential function $a \sim (H_0/D_K)^y$ for $y = -0.7$. Comparison with the exponents $y = -0.3$ or -0.34 recommended by Gestrich and Kraus[13] on basis
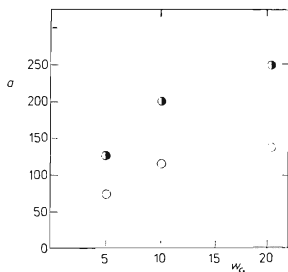

Fig. 1

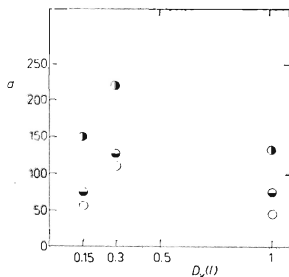Interfacial area a in dependence on superficial gas velocity w_G. $H_0 = 0.3$ m, ○ $D_K = 0.15$, ◑ $D_K = 0.30$ m

Fig. 2

Interfacial area a in dependence on diameter of experimental unit $D_K(l)$. $w_G = 0.05$ m/s, ◑ $H_0 = 0.15$ m, ◕ $H_0 = 0.30$ m, ○ $H_0 = 0.6$ m

of data for deep bubble beds proves our initial assumption on significant effect of bubble bed dimensions on mass transfer characteristics in shallow beds. Dashed lines in Fig. 4 represent data obtained by Mashelkar and Sharma[14] and by Schumpe and Deckwer[2] for $H_0/D_K = 6-7$ (using the method of CO_2 absorption in NaOH solutions). It is apparent from this Fig. that with increasing ratio H_0/D_K interfacial area approaches asymptotically the values corresponding to deep beds.

As to lower values of a observed in the large-scale rectangular unit (Fig. 3) one might be tempted to ascribe the observed decrease of interfacial areas (in comparison with cylindrical columns with $D_K = 0.15$ and 0.30 m) to the existence of marco-scale circulations reported or predicted by some authors[15-17] in medium and large-size units even at conditions of uniform gas distribution. Such macrocirculations would indeed affect negatively gas-holdup and specific interfacial areas so that their effect would have to be considered in design of large-scale units. Our former experimental studies[18,19] performed in units with $D_K = 0.15$ and 0.30 m proved however that the existence of macrocirculation flow-streams could be severely limited by the use of properly designed distributing plates ensuring stable uniform gas distribution at the gas inlet into the bed. The irregular flow patterns observed visually in the rectangular unit (namely at lower gas velocities) can be probably explained rather by properties of the used distributing plate. Due to its relatively small thickness and com-
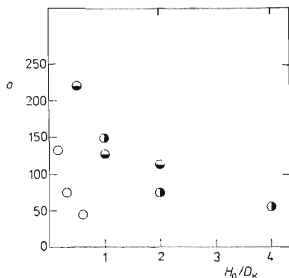

Fig. 3

Interfacial area a in dependence on ratio of clear liquid height to column diameter H_0/D_K . $w_G = 0.05$ m/s, ◑ $D_K = 0.15$ m, ◐ $D_K = 0.30$ m, ○ $l = 1$ m
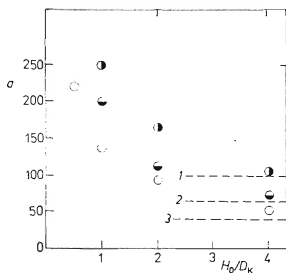
Fig. 4

Interfacial area a in dependence on ratio of clear liquid height to column diameter H_0/D_K. ○ $w_G = 0.05$ m/s, ◕ $w_G = 0.10$ m/s, ◐ $w_G = 0.20$ m/s. ----- limiting value for 1 $w_G = 0.20$ m/s, 2 $w_G = 0.10$ m/s, 3 $w_G = 0.05$ m/s

plicated assembling the plate has not been completely horizontal over the whole cross section and local unevenness could have been responsible for partly nonuniform gas distribution with consequently induced macrocirculations. Beside that, dead spaces might occur in corners of the rectangular unit diminishing experimentally obtained interfacial areas. Thus, according to our opinion, additional experiments in large- -scale units are needed before making final conclusions on the effect of scale-up of bubble bed dimensions on interfacial mass transfer intensity. Indeed provisions have to be made in these experiments to diminish the undesirable effect of secondary factors discussed here. With regard to large dimensions of the units used and thus to their complicated rearrangement it has not been possible to make the suggested arrangements within the frame of this study.

LIST OF SYMBOLS

a	specific interfacial area related to unit of liquid volume (m^{-1})
A	reaction component (CO_2)
B	reaction component (NaOH)
c	concentration ($gmol\, cm^{-3}$)
d_0	diameter of holes of distributing plate (mm)
D_A	diffusivity of compound A
D_K	column diameter (m)
E_i	enhancement factor for instantaneous reaction
H	height of bubbled bed (m)
H_0	clear liquid height (m)
H_A	Henry's law constant for gas A ($atm\, cm^3\, mol^{-1}$)
I	ionic strength ($kg\, ion\, m^{-3}$)
k	reaction rate constant ($m^3\, kmol^{-1}\, s^{-1}$)
k_G	gas side mass transfer coefficient ($mol^{-2}\, s^{-1}\, Pa^{-1}$)
k_L	liquid side mass transfer coefficient ($m\, s^{-1}$)
l_K	length of side of rectangular unit (m)
$M = D_A k c_B / k_L^2$	coefficient in Eqs (2) and (3)
P_A	partial pressure of CO_2 (Pa)
R	rate of absorption ($mol\, m^{-2}\, s^{-1}$)
t	time (s)
T	temperature (K)
w_G	superficial gas velocity ($m\, s^{-1}$)
φ	relative free plate area ratio (%)
μ_{rel}	viscosity of liquid phase related to that of water

Subscripts

av	average
A = CO_2	
B = OH^-	
i	component i
o	initial
S	solution

W   water

∞ infinite dilution

Superscripts

—   mean value

*   value at interface

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