

Mass transfer in electrolytic cells with gas stirring

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Mass transfer to wall electrodes was investigated in a circular cell agitated by gas bubbles. Perforated and porous plates were used as gas spargers. Electrodes with varying height and electrolytic solutions having different physical properties were tested. It was found that the enhancing effect of gas bubbles on the mass transfer coefficient is a function of the gas hold-up, irrespective of the velocity of the gas flow and the gas distributor employed.

The results were correlated for short mass transfer lengths by the relationship

$$Sh = 0.231(ScGa)^{\frac{1}{3}}(L/D_c)^{-0.194} \epsilon^{0.246}$$

and for fully developed mass transfer by

$$Sh_{\infty} = 0.256(ScGa)^{\frac{1}{3}} \epsilon^{0.254}$$

Nomenclature

| | | | |
|----------------------|--------------------------------------------------|---------------------------|-------------------------------------------------------------------------|
| <i>A</i> | surface electrode area (cm ²) | <i>I</i> | (cm) limiting current (A) |
| <i>a</i> | factor in Equations 1 and 4 | <i>k, k_∞</i> | mass transfer coefficient (cm s ⁻¹) |
| <i>b</i> | exponent in Equation 4 | <i>L</i> | electrode height (cm) |
| <i>c</i> | exponent in Equation 4 | <i>Sc</i> | Schmidt number, $Sc = \nu D^{-1}$ |
| <i>C₀</i> | bulk concentration (mol cm ⁻³) | <i>Sh, Sh_∞</i> | Sherwood number, $Sh = kLD^{-1}$; $Sh_{\infty} = k_{\infty}LD^{-1}$ |
| <i>D</i> | diffusivity (cm ² s ⁻¹) | <i>V_s</i> | superficial gas velocity (cm s ⁻¹) |
| <i>D_c</i> | column diameter (cm) | <i>z</i> | axial position (cm) |
| <i>F</i> | Faraday's constant | <i>ε, ε_z</i> | gas holdup |
| <i>g</i> | gravitational acceleration (cm s ⁻²) | <i>μ</i> | dynamic viscosity (g cm ⁻¹ s ⁻¹) |
| <i>Ga</i> | Galileo number, $Ga = L^3 g \nu^{-2}$ | <i>ν</i> | kinematic viscosity (cm ² s ⁻¹) |
| <i>h</i> | liquid level in open tube manometer | <i>ρ</i> | density (g cm ⁻³) |

1. Introduction

Gas stirring of liquids and suspensions is often used in industrial processes. This method of mixing has been proposed for the enhancement of mass transfer and as a means of improving the yield of electrochemical cells [1-3]. Moreover, it allows for a simpler cell design, and the absence of mechanical stirring devices lowers the investment costs.

Two types of electrolytic cell agitated by

bubbles can be distinguished: (a) cells with gas evolving electrodes; (b) cells with gas introduction from the outside.

A great number of studies deal with the problem of mass transfer in cells where the gas is generated by an electrochemical reaction on the electrodes [1, 4-17]. On the other hand, scarce information is available on cells with gas sparging from the outside [2, 18-22].

Although mass transfer rates are higher in cells with gas production at the electrodes than

in cells with gas sparging, it is recognized that the former type of cell presents some limitations. For instance in the electrodeposition of metals, spongy and porous deposits may be produced; this does not happen when an inert gas is introduced from the outside. The present paper deals with this latter type of cell.

In an earlier paper, Ibl [18] showed the feasibility of the use of gas sparging as a suitable method for improving mass transfer in cells. Ettel *et al.* [2], Ismail [19] and Jennings *et al.* [20] working with rectangular, annular and two-phase flow cells, respectively, found that the mass transfer rate increased with increasing gas flow rate.

Ibl *et al.* [11] studied the effect of the superficial gas velocity on the mass transfer coefficient in rectangular cells with porous plates as gas distributors. They found that the gas velocity is the most important variable. However, the experimental results could not be correlated as a single function of the gas velocity independently of the gas distributor employed.

Sigrist *et al.* [21] investigated a rectangular cell with internal (gas lift) and external liquid circulation; the gas was introduced through a vertical porous plate facing the test electrode. They showed that the mass transfer coefficient depends only on the gas void fraction irrespective of the values of the liquid and gas flow rates.

Cavatorta and Böhm [22] studied the effect of gas velocity, gas distributor, gas hold-up and flow regime on the liquid to wall mass transfer in a circular cell. It was found that the gas velocity as well as the gas distributor affect the mass transfer coefficient. However, it was recognized

that the gas hold-up plays an important role in gas sparging systems; the combined effect of both gas velocity and gas distributor could be taken into account in correlating the mass transfer coefficient as a function of the gas hold-up:

$$k = ae^{0.25} \quad (1)$$

where a is a constant for all distributors.

In this paper dimensionless correlations for mass transfer to wall electrodes in electrolytic cells with gas sparging are presented.

2. Experimental details

The experimental set-up is shown schematically in Fig. 1. The electrolytic cell was a circular column, 5 cm in inner diameter and 100 cm high, constructed from a lucite tube. The experiments were carried out with no net liquid circulation, the initial level (gas free) being kept constant at 60 cm.

The gas (nitrogen) was introduced through a sparger placed at the bottom of the column. It was humidified before entering the column to avoid the evaporation of the electrolyte at high gas flow rates. Perforated plates of lucite, all 5 mm thick, and porous plates of sintered glass were used as gas distributors. Tables 1 and 2 show their characteristics.

The limiting current method was used to measure the mass transfer coefficients. The reduction of potassium ferricyanide on a nickel electrode in strong alkaline solutions was used as test reaction. Under limiting current conditions the mass transfer coefficients were evaluated by applying the following equation:

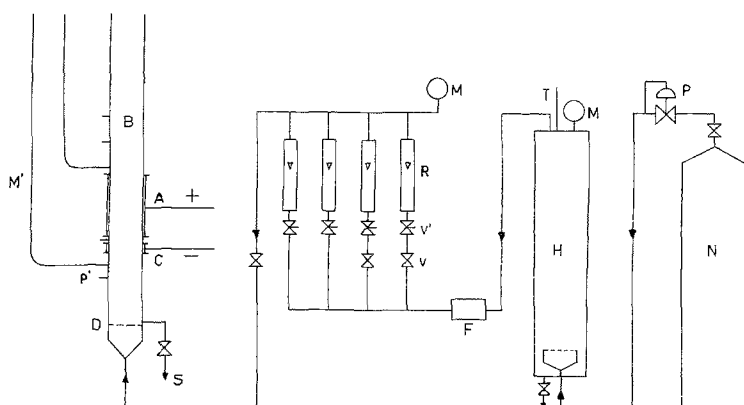


Fig. 1. Experimental set-up. A, Anode; B, column cell; C, cathode; D, gas distributor; F, filter; H, gas saturator; M, Bourdon-type manometer; M', open tube manometer; N, nitrogen tube; P, pressure regulator; P', pressure tap; R, rotameter; S, drain; T, thermometer; V, on-off valve; V', needle valve.

Table 1. Characteristics of porous plates used as distributors

| Porous plate | Thickness (mm) | Diameter (cm) | Pore diameter (μm) |
|--------------|----------------|---------------|---------------------------------|
| D-PM | 5.5 | 5 | 15–30 |
| D-PG | 6.0 | 5 | 30–45 |

$$k = \frac{I}{C_0 A F} \quad (2)$$

The electrolytic solutions employed were all 0.01 M equimolar in potassium ferro- and ferri-cyanide; 0.5 M sodium hydroxide (solution S1) or a 0.4 M equimolar sodium carbonate–bicarbonate buffer (solutions S2 to S8) were used as inert electrolyte. Carboxymethylcellulose–sodium salt (CMC) was added to some solutions (S3 to S8) in order to vary the viscosity.

Table 3 lists the CMC concentration, working temperature and physical properties of the solutions. The viscosity was measured with Ubbelohde-type viscometers, densities were measured with an analytical Mohr balance and diffusion coefficients were obtained by a method developed by Tonini *et al.* [23].

The electrodes were embedded in the column wall. The cathodes were nickel rings, 0.5, 0.9 and 1.79 cm high (L1, L2 and L3); the anode was a nickel-plated copper tube, 14 cm high. The location of the electrodes was based on previous studies of the fluid dynamic behaviour of the column [24], and they were placed in the zone of constant gas hold-up, i.e. at 26.5 cm from the

Table 2. Characteristics of perforated plates used as distributors

| Perforated plate | Hole diameter (mm) | Number of orifices | Distance between orifices (mm) | Layout |
|------------------|--------------------|--------------------|--------------------------------|--------|
| D1/2 | 0.5 | 1 | | (a) |
| D1 | 1 | 1 | | (a) |
| D1/2-6 | 0.5 | 6 | 13 | (b) |
| D1-8 | 1 | 8 | 10 | (b) |
| D1/2-8 | 0.5 | 8 | 10 | (b) |
| D1-17 | 1 | 17 | 4.5 | (b) |
| D1/2-18 | 0.5 | 18 | 4.5 | (c) |
| D1-21 | 1 | 21 | 10 | (c) |
| D1/2-21 | 0.5 | 21 | 10 | (c) |

(a), Single central orifice; (b), circle at 12.5 mm from column axis; (c), square layout.

sparger in the cathode and at 35.5 from the sparger in the anode.

Open-tube manometers filled with the electrolytic solution were connected to several pressure taps placed along the wall of the column. The liquid levels in the manometers allowed the determination of the gas hold-up by the well-known manometric method:

$$\varepsilon_z = \frac{dh}{dz} \Big|_z \quad (3)$$

3. Results and discussion

Fig. 2 shows experimental results, plotted as k versus V_s , for the electrode L2 and solution S1. In the same figure the gas hold-up in the mass

Table 3. Solution properties

| Solution | CMC conc. (g per 100 ml) | T ($^{\circ}\text{C}$) ^a | ρ (g cm^{-3}) | $\mu \times 10^2$ ($\text{g cm}^{-1} \text{s}^{-1}$) | $D \times 10^6$ ($\text{cm}^2 \text{s}^{-1}$) | Sc |
|----------|--------------------------|---------------------------------------|-------------------------------|--------------------------------------------------------|-------------------------------------------------|-------|
| S1 | – | 21.8 | 1.024 | 1.07 | 6.12 | 1707 |
| S2 | – | 25.5 | 1.064 | 1.20 | 5.51 | 2047 |
| S3 | 0.10 | 23.0 | 1.068 | 1.93 | 5.15 | 3509 |
| S4 | 0.15 | 22.1 | 1.069 | 2.32 | 5.04 | 4306 |
| S5 | 0.20 | 23.0 | 1.069 | 2.80 | 5.16 | 5076 |
| S6 | 0.30 | 25.4 | 1.068 | 3.44 | 5.52 | 5835 |
| S7 | 0.45 | 23.0 | 1.070 | 6.38 | 5.15 | 11578 |
| S8 | 0.60 | 23.0 | 1.069 | 9.96 | 5.14 | 18127 |

^a Temperature control, $\pm 0.5^{\circ}\text{C}$.

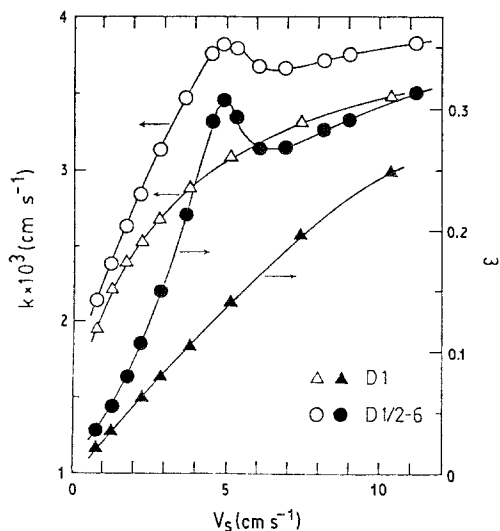


Fig. 2. Effect of superficial gas velocity and gas distributor on the mass transfer coefficient and gas hold-up.

transfer region was plotted as a function of V_s . For a given superficial gas velocity both the mass transfer coefficient and the gas hold-up depend on the distributor employed.

As can be seen, the superficial gas velocity affects the mass transfer rate as well as the gas hold-up in the same way. It is shown that the higher the gas void fraction the higher is the mass transfer coefficient; a reduction of the gas hold-up is accompanied by a decrease of the coefficient.

These facts suggest the establishment of an expression relating the mass transfer coefficient to gas hold-up, independently of the gas distributor. This relation is shown in Fig. 3 where the k values obtained with different distributors are plotted versus the gas hold-up.

Fig. 4 shows some typical values of k obtained with different electrolytic solutions. Data analysis

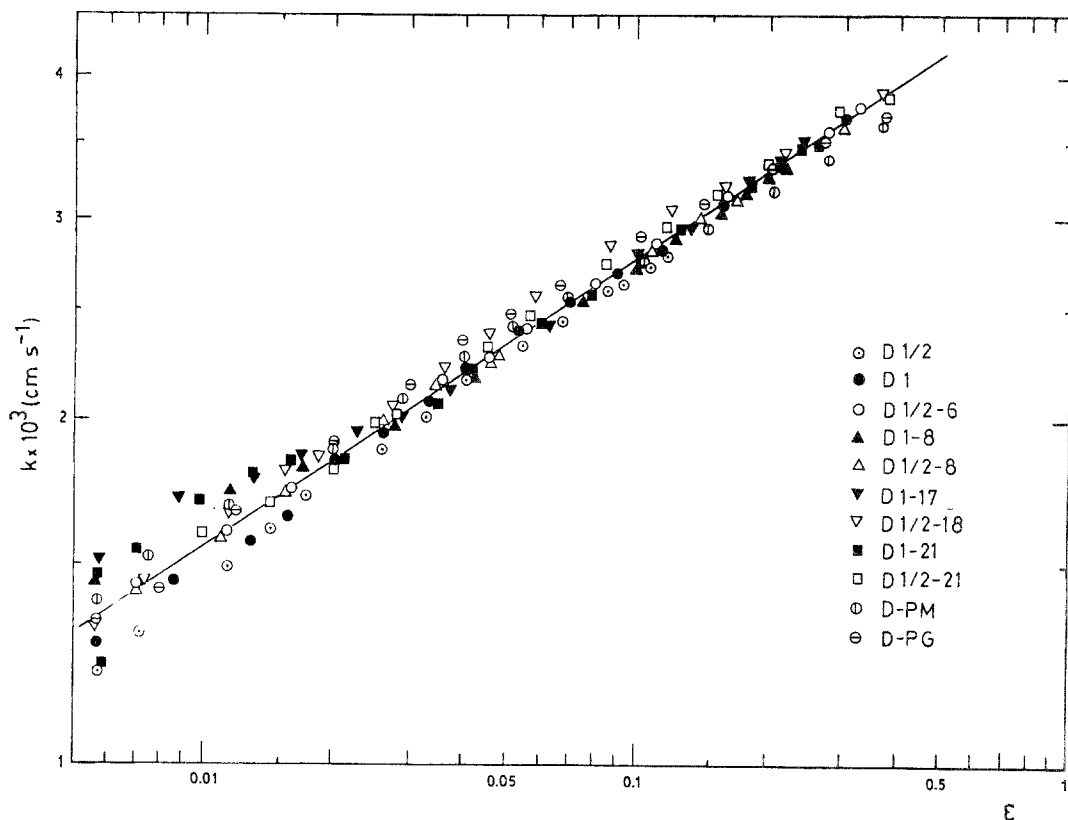


Fig. 3. Mass transfer coefficient as function of gas hold-up for Electrode L2 and solution S1.

Table 4. Effect of mass transfer length

| Electrode | Height (cm) | Correlation | S.D. |
|-----------|----------------|---------------------------------------------------|------|
| L1 | 0.5 | $Sh = 0.363(ScGa)^{\frac{1}{3}} \epsilon^{0.245}$ | 2.1% |
| L2 | 0.9 | $Sh = 0.322(ScGa)^{\frac{1}{3}} \epsilon^{0.246}$ | 2.4% |
| L3 | 1.79 | $Sh = 0.287(ScGa)^{\frac{1}{3}} \epsilon^{0.248}$ | 2.4% |

suggests that the k/D relation increases when the product Dv decreases. Taking account of this, and in order to obtain a dimensionless relationship, the experimental values were correlated as

$$Sh = a(ScGa)^b \epsilon^c \quad (4)$$

According to the suggestion of Sigrist *et al.* [21] the value of 'b' was taken as $\frac{1}{3}$; Fig. 5 shows a sample of data plotted as $Sh/(ScGa)^{\frac{1}{3}}$ versus ϵ for electrode L2.

It is found that Equation 4 adequately describes the influence of the physical properties with $b = \frac{1}{3}$, but the factor 'a' depends on the electrode height. Table 4 summarizes the results for the three electrodes tested. As can be seen, the mass transfer coefficient decreases with increasing mass transfer length (electrode height). This fact can be explained by assuming that the mass transfer occurs through a concentration boundary layer. In bubble columns with no net liquid circulation, the liquid rises in

the core zone and moves down again near the wall. A boundary layer develops on the wall electrode and its thickness increases until the turbulent eddies avoid further growth [25].

Since the greater the thickness of the boundary layer the lower is the local mass transfer coefficient, the average coefficient decreases with increase in the electrode height. However, the local coefficient reaches a constant value (k_{∞}) for fully developed mass transfer, which has the practical consequence that the mass transfer rate no longer depends on the electrode height.

Following Surgenor *et al.* [26], fully developed mass transfer coefficients were obtained by differencing the limiting currents measured by the electrodes L2 and L3 at the same flow conditions:

$$k_{\infty} \cong \frac{I_{L3} - I_{L2}}{C_0(A_{L3} - A_{L2})F} \quad (5)$$

The k_{∞} values were correlated in dimensionless form as a function of $(ScGa)$ and ϵ according to

$$Sh_{\infty} = 0.256(ScGa)^{\frac{1}{3}} \epsilon^{0.254} \quad (6)$$

with a standard deviation of 5%. Fig. 6 shows Equation 6 together with the experimental values.

In order to obtain a generalized correlation for short mass transfer lengths the relation L/D_c was introduced as a geometric factor, since on the basis of a circulation cell model for bubble

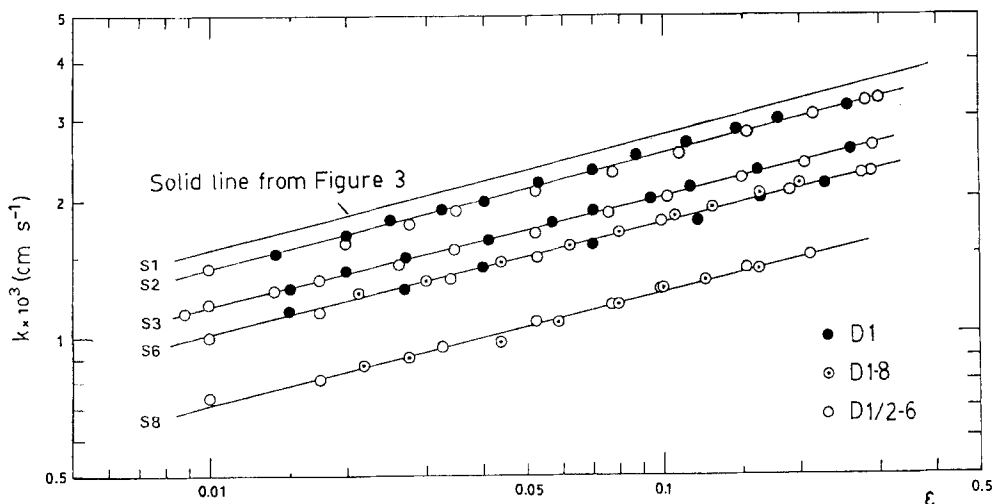


Fig. 4. Effect of liquid properties on the mass transfer coefficient for Electrode L2.

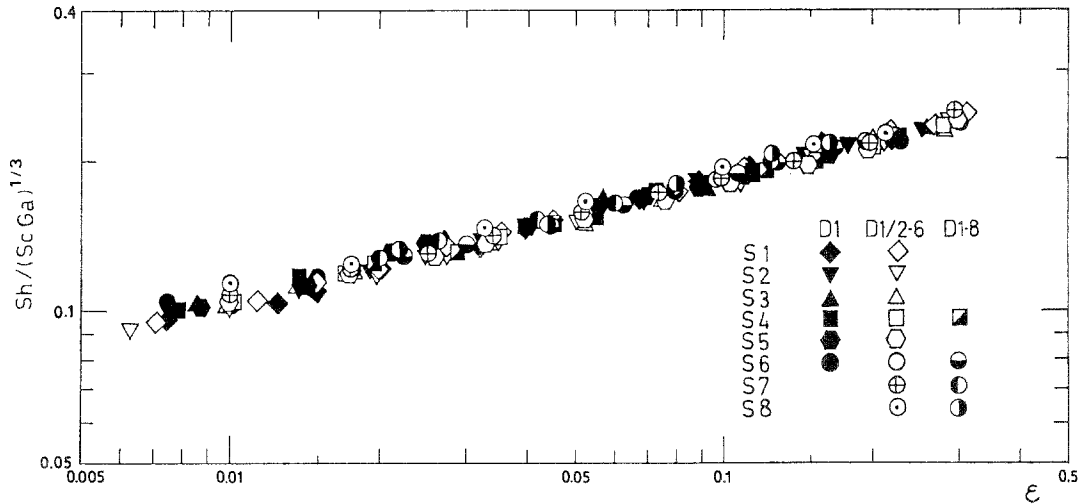


Fig. 5. Plot of $Sh/(ScGa)^{1/3}$ versus gas hold-up.

columns [27] the column diameter (D_c) seems to be a pertinent parameter.

All the experimental data for electrodes L1, L2 and L3 were correlated as

$$Sh = 0.231 (ScGa)^{1/3} (L/D_c)^{-0.194} \varepsilon^{0.246} \quad (7)$$

with a standard deviation of 2.7%.

Equation 7 was obtained for the following range of conditions:

$$0.1 \leq L/D_c \leq 0.36$$

$$6.8 \times 10^8 \leq ScGa \leq 8.8 \times 10^{10}$$

$$0.0025 \leq \varepsilon \leq 0.5$$

$$0.08 \leq V_s \leq 10.0$$

From Equations 6 and 7 it appears that spargers which produce higher gas hold-up are preferred in order to ensure a favourable increase of the mass transfer in electrolytic cells. For a given gas velocity, higher gas voidages and therefore higher mass transfer rates are achieved with multi-orifice plates with small hole diameters (less than 1 mm) or with porous plate distributors [24, 28].

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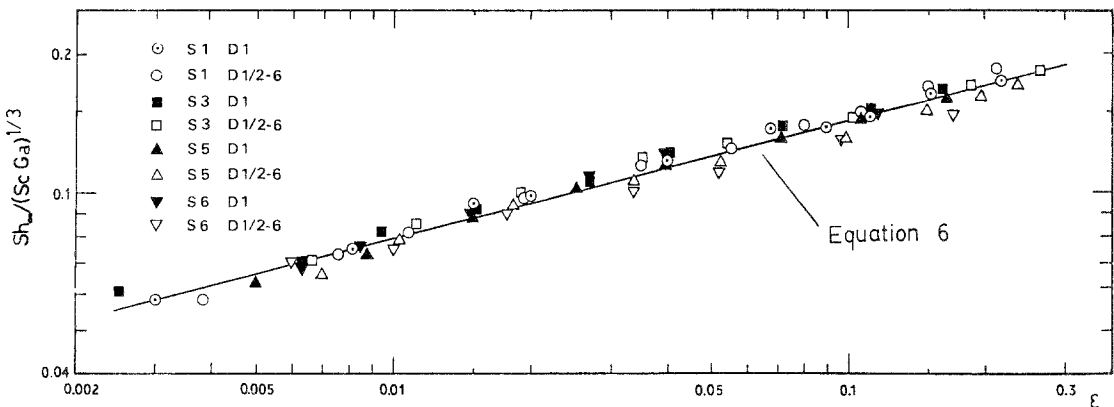


Fig. 6. Fully developed mass transfer correlation.

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