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Enhancement of mass transfer at a spherical electrode in pulsating flow*

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The effect of pulsation on the overall mass transfer coefficient between a sphere and a liquid at low Reynolds number ($Re < 6.36$) has been studied. When there is no flow reversal, pulsations have a negative effect on the mass transfer coefficient, it being minimum when the dimensionless group $\alpha = a\omega/u_0 = 1$. When flow reversal occurs the mass transfer coefficient increases with both frequency, f, and amplitude, a, of the pulse and decreases with the mean fluid velocity, u_0. The variation of the mass transfer coefficient has been studied with a model based on the quasisteady-state assumption. In this way two correlations have been obtained for the mass transfer coefficient:

$$Re < 20 \qquad Sh = 1.23Sc^{1/3}Re^{0.23}$$
$$Re > 20 \qquad Sh = 0.39Sc^{1/3}Re^{0.58}$$

List of symbols

a	amplitude (m)
A, A'	dimensionless constants
B, B'	dimensionless constants
C	bath concentration (mol m^{-3})
d	reactor diameter (m)
d_P	electrode diameter (m)
D	diffusivity of the diffusing ion (m^2 s^{-1})
f	frequency (s^{-1})
I	current (A)
k_0	mass transfer coefficient without pulsation (m s^{-1})
k	instantaneous mass transfer coefficient (m s^{-1})
$\overline{k}$	time-averaged mass transfer coefficient (m s^{-1})
Re	Reynolds number ($u_0 d_P/\nu$)
Re_0	peak Re ($d_P a\omega/\nu$)
Re_C	Critical Re
Re_P	pulsating Re ($d_P(\omega\rho/\mu)^{1/2}$)
Re_V	vibrational Re ($4afd/\nu$)
$\overline{Re}$	time-averaged Re
Sc	Schmidt number (ν/D)
Sh	Sherwood number ($k_0 d_P/D$)
$\overline{Sh}$	time-averaged Sh
t	time (s)
t_i	times where velocity reach the critical value (s)
T	pulsation period (s)
u	instantaneous fluid velocity (m s^{-1})
u_0	mean fluid velocity (m s^{-1})
u_C	critical velocity (m s^{-1})
$\overline{u}$	time averaged fluid velocity (m s^{-1})

Greek letters

α	dimensionless velocity ($a\omega/u_0$)
ϵ	void fraction
ν	kinematic viscosity (m^2 s^{-1})
ρ	fluid density (kg m^{-3})
ω	pulsation (rad s^{-1})

1. Introduction

To increase the mass transfer by convection between a solid wall and a liquid, it is important to increase the turbulence in the proximity of the exchange surface. With the purpose of inducing turbulence in the fluid, some authors propose to subject the solid phase or the liquid phase to mechanical [1–5] or electrical [5–7] disturbances. The effects of mechanical pulsations or vibrations on the mass or heat transfer between a solid and a liquid have been a controversial topic. In general, the different results obtained can be explained because the effect of pulsations depends on the system geometry, hydrodynamic conditions and pulsation characteristics [8].

The increase in turbulence by flow pulsation can only play a relevant role when natural turbulence is not significant. So it is in laminar or transition flow when the use of such disturbances is interesting. At high Reynolds number, turbulence can be so

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significant that the effect of pulsations is masked [9]. Flow pulsations can also cause a long residence time at low Reynolds numbers [10].

Different parameters have been proposed to represent in an empirical way the effect of pulsations on the mass transfer coefficient at different Reynolds numbers. For packed beds, in the study of the electrochemical deposition of copper, the dimensionless velocity, $\alpha = a\omega/u_0$ and the pulse Reynolds, $Re_P = d_P(\omega\rho/\mu)^{1/2}$ has been used [4], and in pulsative flow bioreactors, the peak Reynolds number $Re_0 = (d_P a\omega/\nu)$ was used [10, 11]. On the other hand, in the study of the mass transfer between a sphere and a liquid in pulsating flow at high Reynolds number, the vibrational Reynolds number, $Re_V = d(4af)/\nu$, [8, 12], or a function of it [1, 8, 13–15], has been employed.

This paper deals with the effect of flow pulsations on the mass transfer coefficient between a sphere and a liquid at low Reynolds number, measured electrochemically. The effect of pulsation is studied by varying the frequency and amplitude of pulsations at different fluid velocities. To predict the experimental data theoretically a model based on the quasisteady-state assumption has been developed.

2. Experimental details

The electrodeposition of copper on a spherical copper probe from an acid copper sulphate bath at 20° C was used for the mass transfer measurements. The bath concentration, C, was 7.87×10^{-3} M $CuSO_4$ and 1 M H_2SO_4; it was prepared by dissolving ACS certified reagent grade chemicals into the distilled water. The physical properties of the electrolyte at 20° C were: density, $\rho = 1063\,\mathrm{kg\,m^{-3}}$, kinematic viscosity as determined using an Ostwald viscometer, $\nu = 1.146 \times 10^{-6}\,\mathrm{m^2\,s^{-1}}$, diffusivity of Cu^{2+} ion, $D = 6 \times 10^{-10}\,\mathrm{m^2\,s^{-1}}$ [4].

A diagram of the experimental arrangement is shown in Fig. 1. The apparatus consisted of a 86.3 mm diameter Plexiglass tube; a 6 mm diam. spherical copper probe, acting as working electrode was placed in the centre of the tube, it being held by a 1 mm diam. steel tube insulated from the solution by polymer film. A plastic capillary placed inside the holding tube was used as a Luggin probe for the reference electrode. The anode was a 75 mm diam. platinum circular grid placed 50 mm above the cathode. Below the cathode was a 100 mm long section packed with 3 mm diam. glass spheres to ensure uniform liquid distribution.

The pulsating mechanism was made up of a deformable PTFE membrane inside a tube with the same diameter as the reactor which acted as a piston. The motor rotational motion was transformed into translation motion by a crankshaft system. In order to convert the cyclic output of the transmission into a back-and-forth movement for the piston, a coupling mechanism was used. The pulsation amplitude was modified by changing the length of the connecting rod. The pulsation frequency was modified by changing the motor rotation speed.

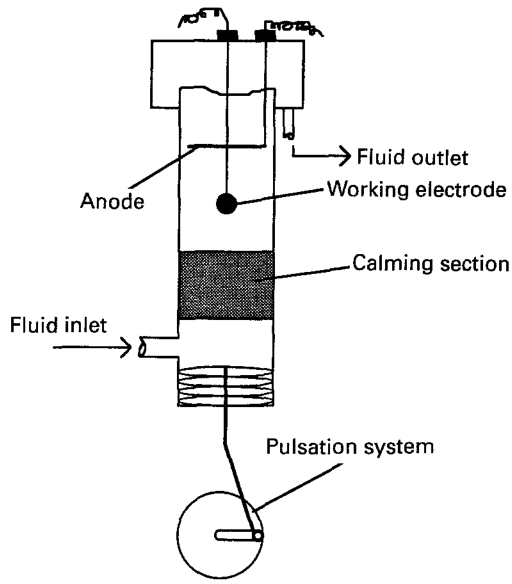

Fig. 1. Experimental arrangement.

Runs were made by operating at diffusion limiting current, keeping the working electrode potential at −300 mV vs Ag/AgCl in 3 M KCl as reference electrode, using a potentiostat (Tacussel type PJT-120-1). The major independent variables investigated were flow velocity, u, pulsation frequency, f, and pulsation amplitude, a, which were varied in the limits: $4 \times 10^{-4}\,\mathrm{m\,s^{-1}} \le u \le 1.2 \times 10^{-3}\,\mathrm{m\,s^{-1}}$; $1\,\mathrm{mm} \le a \le 8.925\,\mathrm{mm}$; $0\,\mathrm{s^{-1}} \le f \le 1\,\mathrm{s^{-1}}$.

3. Background

When a periodic pulsation is imposed on a steady flow, the flow hydrodynamic characteristics are very different to those at steady flow, and to those at periodic pulsation in the absence of flow. For steady flow, the mass transfer coefficient is of the form:

$$k_0 = A{u_0}^B \tag{1}$$

where k_0 is the mass transfer coefficient in steady flow, u_0 is the mean fluid velocity. A and B are two constants depending on the hydrodynamic characteristics and solution properties.

Table 1 shows some mass transport correlations in steady flow for different Reynolds numbers. From these correlations it can be seen that there is a critical Reynolds number, $Re_C \cong 20$, below which B varies from 0.2 to 1/3, and above which B varies from 1/2 to 2/3. Jenson [23] has shown theoretically that this change due to the hydrodynamic regime occurs at $Re = 17$. Garner and Grafton [24], for solid spheres, found $Re_C = 40$ to 50, whereas Garner and Skeland [25] observed this change for $Re_C = 18$ to 23.

In pulsating flow, according to the value of the dimensionless velocity, α, a flow reversal can occur for a time, t, lower than a semiperiod: $t < T/2$, when $\alpha > 1$. At first, the flow direction does not exert any influence on the mass transfer coefficient, so the

Table 1. Mass transport correlations in steady flow

Author	*System*	*Particle*	*Correlation*	*Range*
Jolls (1969) [16]	Reduction of ferricyanide	Sphere	$Sh = 1.59Sc^{1/3}Re^{0.56}$	$Re > 140$
			$Sh = 1.44Sc^{1/3}Re^{0.58}$	$35 < Re < 140$
Karabelas (1971) [17]	Reduction of ferricyanide	Sphere	$Sh = 4.58Sc^{1/3}Re^{1/3}$	$0.05 < Re < 30$
Gibert (1971) [18]	Reduction of ferricyanide	Sphere	$Sh = 0.882Sc^{1/3}Re^{0.452}$	$400 < Re < 1250$
			$Sh = 0.447Sc^{1/3}Re^{0.538}$	$1250 < Re < 12\,500$
Coeuret (1976) [19]	Reduction of ferricyanide	Spheres bed	$Sh = 5.4Sc^{1/4}Re^{1/3}$	$0.04 < Re < 30$
				$\epsilon = 0.413$
				$1700 < Sc < 11\,000$
Dwidedi (1977) [20]	General correlation		$\epsilon\, Sh = 1.1Sc^{1/3}Re^{0.28}$	$Re < 10$
			$\epsilon\, Sh = 0.45Sc^{1/3}Re^{0.59}$	$Re > 10$
Gaunad (1978) [21]	Reduction of ferricyanide	Spheres bed	$Sh = 3.28Sc^{1/3}Re^{0.326}$	$0.2 < Re < 7$
				$\epsilon = 0.42$
Lacoste (1979) [22]	Reduction of Cu^{2+}	Spheres bed	$Sh = 4.3Sc^{1/4}Re^{0.35}$	$0.1 < Re < 3$

representative magnitude of flow will be the modulus of the instantaneous velocity. Thus,

$$|u| = |u_0 + a\omega \sin(\omega t)| \tag{2}$$

where u is the instantaneous fluid velocity, and $\omega = 2\pi f$.

So far the quasisteady-state approach has been used in the study of the effect of pulsation on heat transfer [26]. In this approach, the time-averaged transfer coefficient in pulsating flow is obtained from the instantaneous coefficient calculated from steady-flow relationships. In the present case, the time averaged mass transfer coefficient, assuming a sinusoidal variation of velocity, can be written as

$$\bar{k} = A\left[\frac{1}{T}\int_0^T |u_0 + a\omega\sin(\omega t)|^B \,\mathrm{d}t\right] \tag{3}$$

where $\bar{k}$ is the time averaged mass transfer coefficient and T is the pulsation period (pulsation cycle time interval).

It is necessary to include a modulus sign in the integral in Equation 3 to allow it to have a real value when the dimensionless velocity, α, exceeds unity, i.e., when the flow reverses for part of the cycle. The enhancement of the mass transfer coefficient can be represented by the ratio of the time averaged mass transfer coefficient in pulsating flow $\bar{k}$, and the mass transfer coefficient in steady flow, k_0, at the same fluid velocity, $\bar{k}/k_0$.

Since the exponent of velocity in Equation 1 depends on the Reynolds number, and the instantaneous velocity changes throughout a period, we should know when the Reynolds number exceeds this critical value, Re_C. In the most general case, and taking into account that, in our experimental conditions the maximum steady Re is 6.36, less than $Re_C \cong 20$ (Table 1), it is possible to obtain four times this instantaneous critical value of velocity, u_C, over a pulsation period. Figure 2 shows a typical variation of the absolute value of instantaneous velocity with time over a pulsation period. From this Figure, and Equation 2, the times at which velocity reaches this critical value are given by:

$$\begin{aligned} t_1 &= \frac{1}{\omega}\arcsin\left(\frac{u_C - u_0}{a\omega}\right) \\ t_2 &= \frac{T}{2} - t_1 \\ t_3 &= \frac{T}{2} + \frac{1}{\omega}\arcsin\left(\frac{u_C + u_0}{a\omega}\right) \\ t_4 &= \tfrac{3}{2}T - t_3 \end{aligned} \tag{4}$$

The application of the quasisteady-state model has been developed as follows. Taking into account that the parameters A and B vary with the Reynolds number, Equation 3 can be developed thus:

$$\begin{aligned} \bar{k} = \frac{1}{T}\Bigg[& A\int_0^{t_1} |u_0 + a\omega\sin(\omega t)|^B \,\mathrm{d}t \\ & + A'\int_{t_1}^{t_2} |u_0 + a\omega\sin(\omega t)|^{B'} \,\mathrm{d}t \\ & + A\int_{t_2}^{t_3} |u_0 + a\omega\sin(\omega t)|^B \,\mathrm{d}t \\ & + A'\int_{t_3}^{t_4} |u_0 + a\omega\sin(\omega t)|^{B'} \,\mathrm{d}t \\ & + A\int_{t_4}^{T} |u_0 + a\omega\sin(\omega t)|^B \,\mathrm{d}t\Bigg] \end{aligned} \tag{5}$$

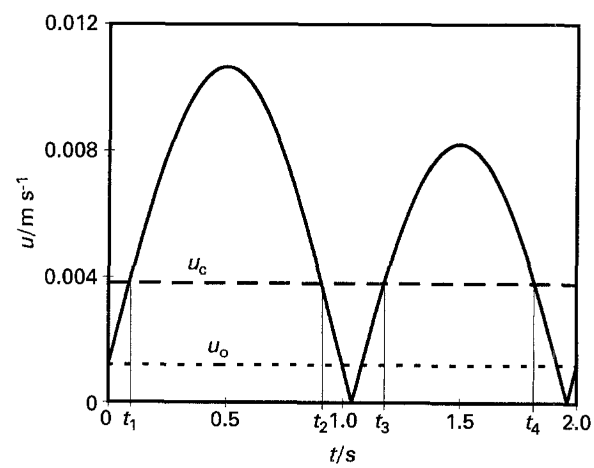

Fig. 2. Variation of instantaneous fluid velocity with time over a pulsation period. $f = 0.5\,\mathrm{s^{-1}}$, $a = 3\,\mathrm{mm}$, $u_0 = 1.2 \times 10^{-3}\,\mathrm{m\,s^{-1}}$, $u_C = 3.82 \times 10^{-3}\,\mathrm{m\,s^{-1}}$.

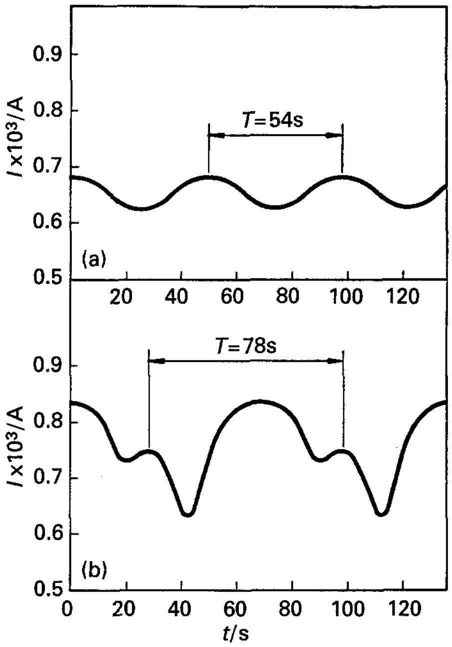

Fig. 3. Experimental variation of current with time. (a) $u_0 = 4 \times 10^{-4}\,\mathrm{m\,s^{-1}}$, $a = 1\,\mathrm{mm}$, $T = 54\,\mathrm{s}$, $\alpha = 0.29$. (b) $u_0 = 4 \times 10^{-4}\,\mathrm{m\,s^{-1}}$, $a = 8.925\,\mathrm{mm}$, $T = 78\,\mathrm{s}$, $\alpha = 1.8$.

where A and B are the parameters corresponding to Equation 3 for $Re < Re_C$, and A' and B' are those corresponding to $Re > Re_C$. The values of t_1, t_2, t_3, t_4, can be obtained from Equation 4.

The numerical solution of Equation 5 for any value of A, A', B, B' and Re_C allows a certain value of $\bar{k}$ to be obtained. The best values of coefficients A, A', B, B' and Re_C can be obtained from the least-square regression fitting of all experimental data using the Marquardt algorithm. The agreement between the values of A, A', B, B' and Re_C obtained by this method and those from the literature enable the appropriateness of the proposed model to be verified.

4. Results

Figure 3 shows the variation of current with time. For small frequencies when there is no flow reversal, $\alpha < 1$, the current varies sinusoidally, with the same frequency of flow pulsation. For high frequencies, if flow reversal occurs, $\alpha > 1$, the current reaches two maxima and two minima in one pulsation cycle. This behaviour agrees with the assumption that flow direction does not exert any influence on the mass transport process.

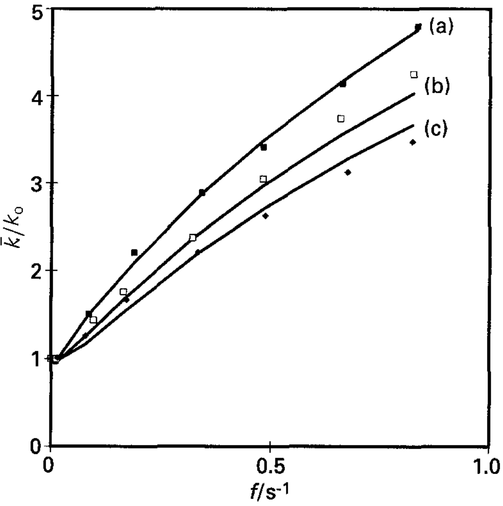

Fig. 5. Variation of ratio $\bar{k}/k_0$ with frequency for different values of fluid velocity. $a = 3\,\mathrm{mm}$. (a) $u_0 = 4 \times 10^{-4}\,\mathrm{m\,s^{-1}}$; (b) $u_0 = 8 \times 10^{-4}\,\mathrm{m\,s^{-1}}$; (c) $u_0 = 1.2 \times 10^{-3}\,\mathrm{m\,s^{-1}}$. Key: (◆, □, ■) experimental data; (——) quasisteady-state model.

To illustrate the effect of flow pulsations on mass transfer, Figures 4 and 5 show the ratio $\bar{k}/k_0$ against frequency for different values of amplitude and velocity, respectively, where the ratio $\bar{k}/k_0$ represents the enhancement of mass transfer. These Figures show that for small frequencies, pulsation has a negative effect on the mass transfer, this decrease in the mass transfer being less than 10%. For high frequencies, when flow reversal occurs, a large increase in the mass transfer rate is observed, so that, for a given frequency, the enhancement of mass transfer increases with increasing amplitude of the pulsation and with decreasing of velocity. Similar results have been observed in β-naphthol dissolution in a packed

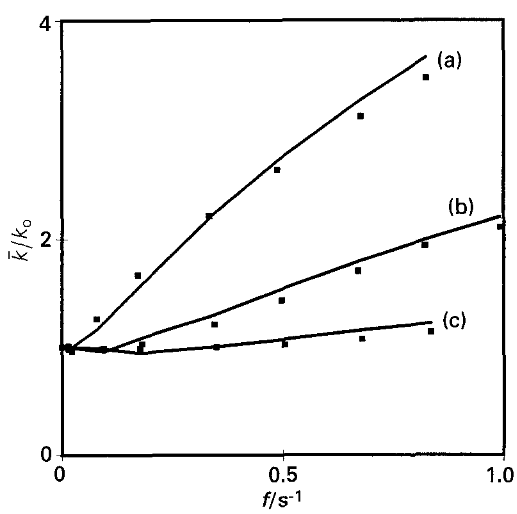

Fig. 4. Variation of ratio $\bar{k}/k_0$ with frequency for different values of amplitude. $u_0 = 1.2 \times 10^{-3}\,\mathrm{m\,s^{-1}}$. (a) $a = 8.925\,\mathrm{mm}$; (b) $a = 3\,\mathrm{mm}$; (c) $a = 1\,\mathrm{mm}$. Key: (■) experimental data; (——) quasisteady-state model.

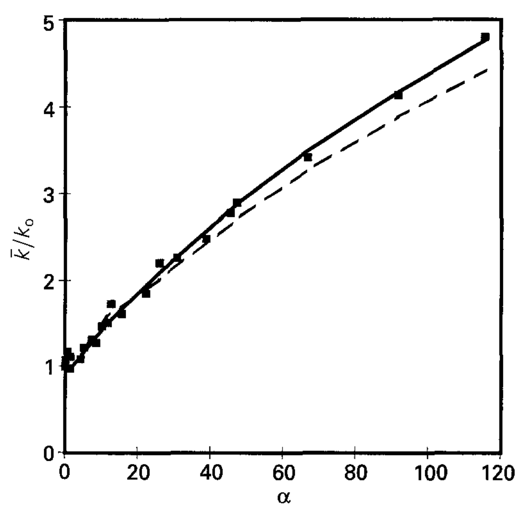

Fig. 6. Variation of ratio $\bar{k}/k_0$ against dimensionless velocity, α, for different values of amplitude. $u_0 = 1.2 \times 10^{-3}\,\mathrm{m\,s^{-1}}$. Key: (■) experimental data; (——) quasisteady-state model; broken line: Equations 8–10.

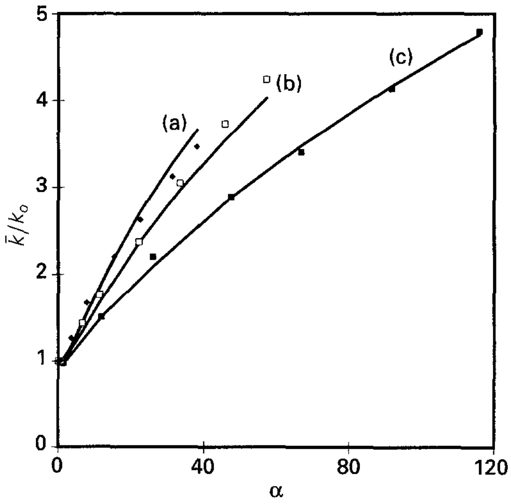

Fig. 7. Variation of ratio $\bar{k}/k_0$ with dimensionless velocity, α for different values of fluid velocity. $a = 8.925$ mm. (a) $u_0 = 4 \times 10^{-4}\,\mathrm{m\,s^{-1}}$; (b) $u_0 = 8 \times 10^{-4}\,\mathrm{m\,s^{-1}}$; (c) $u_0 = 1.2 \times 10^{-3}\,\mathrm{m\,s^{-1}}$. Key: (◆, □, ■) experimental data; (——) quasisteady-state model.

bed [2, 3], in an electrochemical bed reactor using a copper solution [4], in dissolution of a sphere of benzoic acid [27], and in heat transfer in a double-pipe heat exchanger [28].

Figures 6 and 7 show the variation of $\bar{k}/k_0$ with dimensionless velocity, α, for different values of amplitude and velocity, respectively. For values of $\alpha < 1$, the ratio $\bar{k}/k_0 < 1$, and for $\alpha = 1$, it is minimum. For values of $\alpha > 1$, pulsation has a beneficial effect on mass transfer. Figure 6 shows that for a given value of velocity, the parameter α can be taken as a representative factor for the pulsation effect. On the other hand, as can be seen in Fig. 7, the ratio $\bar{k}/k_0$ decreases when the velocity increases for a given value of α.

5. Discussion

Applying the model based on the quasisteady-state assumption, and using the Marquardt algorithm for the least-square regression fitting for all experimental data, the results obtained are: $Re_C = 20$, $A = 1.10 \times 10^{-5}$, $B = 0.23$, $A' = 6.82 \times 10^{-5}$ and $B' = 0.58$.

Thus, with the values of the sphere diameter, kinematic viscosity and diffusivity, two correlations can be written for mass transport:

$$\text{For } Re < 20\text{: } Sh = 1.23 Sc^{1/3} Re^{0.23} \tag{6}$$

$$\text{For } Re > 20\text{: } Sh = 0.39 Sc^{1/3} Re^{0.58} \tag{7}$$

Figure 8 shows a comparative study of mass transfer for different correlations used in steady-flow conditions and those obtained using the model based on the quasisteady-state assumption. There is good agreement among the literature correlations and those obtained using the model developed here.

Another way of predicting experimental values of the mass transfer coefficient using the quasisteady-state assumption, is to use literature correlations corresponding to steady-state conditions, and to calculate the time-averaged mass transfer coefficient from Equation 5. From Table 1, the following correlations for mass transfer between a sphere and a liquid into an inert-particle bed reactor have been selected:

Karabelas [17] $Sh = 4.58 Sc^{1/3} Re^{1/3}$ $\quad 0.05 < Re < 30$ (8)

Jolls [16] $Sh = 1.44 Sc^{1/3} Re^{0.58}$ $\quad 35 < Re < 140$ (9)

Jolls [16] $Sh = 1.59 Sc^{1/3} Re^{0.56}$ $\quad 140 < Re < 1100$ (10)

In these correlations, Re is the Reynolds number based on the empty reactor and the particle diameter; therefore, in order to use them the void fraction, $\epsilon = 0.41$ must be considered to calculate the real instantaneous fluid velocity.

Figure 6 shows a comparative plot of the ratio $\bar{k}/k_0$

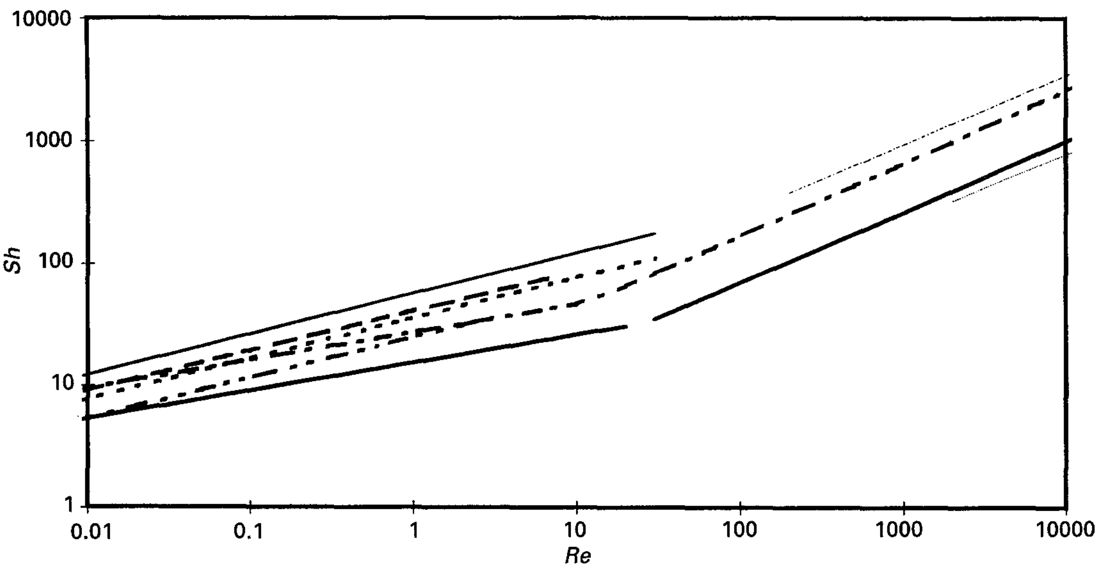

Fig. 8. Comparative study of different mass transfer correlations used in steady flow conditions. (——) quasisteady-state model, (— · — · —) Jolls, (——) Karabelas, (·········) Gibert, (· · · · · ·) Coeuret, (— · —) Dwidedi, (— — —) Gaunad and (— ·· —) Lacoste.

against frequency for experimental data for the quasisteady-state assumption, and for steady-state conditions (Equations 8–10), indicating a good agreement between the proposed model and experimental data.

From the above results it can be seen that the quasisteady-state assumption allows prediction of the experimental values of averaged mass transfer coefficient successfully when pulsation is imposed on a steady flow. Nevertheless, the mathematical procedure is time consuming; hence, it is interesting to use a similar expression to those for steady-state ($Sh = A\,Re^B Sc^C$) based on correlating the time-averaged *Sh* number, $\overline{Sh} = \overline{k}d/D$, with the time-averaged *Re* number, $\overline{Re} = |\overline{u}|d_P/\nu$. This procedure can be justified because in the range of velocities studied, $\overline{|u|^B}$ is approximately equal to $|\overline{u}|^B$ for $B < 1$ with an error less than 10%.

This time-averaged Reynolds number has been used by Hersey [29] in the experimental study of the transition from laminar to turbulent flow for sinusoidal flow of water in rigid tubes, and to correlate experimental results of mass transfer in pulsating flow at zero mean flow velocity. Figure 9 shows a comparison of least-square fitting of experimental average *Sh* number, $\overline{Sh}$, and those obtained from Equations 6 and 7 (quasisteady-state model) versus the time-averaged Reynolds number, $\overline{Re}$. The experimental data fit the following correlations:

$$\text{For } Re < 20\text{: } Sh = 1.23 Sc^{1/3} Re^{0.21} \quad (11)$$

$$\text{For } Re > 20\text{: } Sh = 0.46 Sc^{1/3} Re^{0.53} \quad (12)$$

There is good agreement between Equations 11 and 12 and Equations 6 and 7, respectively. Hence, the approximation $\overline{|u|^B}$ to $|\overline{u}|^B$ for $B < 1$ is valid.

6. Conclusions

(i) Flow pulsation imposed on a steady flow has a beneficial effect on the mass transfer coefficient at low Reynolds numbers, producing an increase of 500% at frequencies of $1\,s^{-1}$ and amplitudes of 8.925 mm, in contrast to the slight increase obtained by other authors working at high Reynolds numbers.

(ii) The effect of pulsations on the mass transfer increases with amplitude and frequency, and when the mean flow velocity decreases.

(iii) Flow pulsation has a negative effect on the mass transfer when the dimensionless velocity, α, is less than 1, and there is no flow reversal.

(iv) At low Reynolds numbers, the quasisteady-state model predicts the effect of pulsations on the mass transfer rate successfully.

(v) Time-averaged mass transfer in pulsating flow can be correlated in terms of the dimensionless groups (Sh, Sc, Re), using time-averaged fluid velocity.

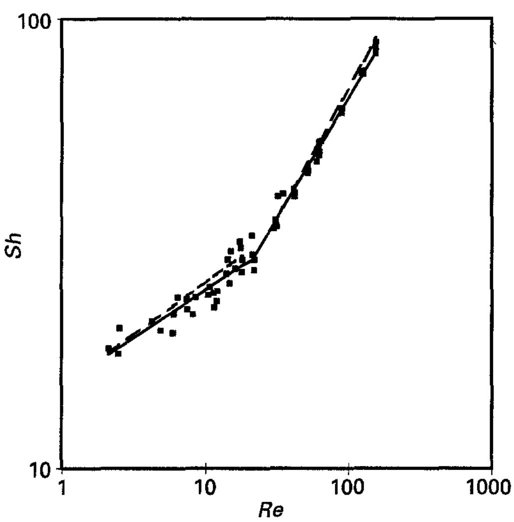

Fig. 9. Time-averaged Sherwood number against time-averaged Reynolds number. Key: (■) experimental data; (——) quasi-steady-state model; broken lines: least-square fitting of experimental data.

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References

[1] H. Gibert and H. Angelino, *Int. J. Heat Mass Transfer* **17** (1974) 625.
[2] J. H. Krasuk and J. M. Smith, *Chem. Eng. Sci.* **18** (1963) 591.
[3] Idem, *AIChE J.* **10** (1964) 759.
[4] A. Ratel, P. Duverneuil and G. Lacoste, *J. Appl. Electrochem.* **18** (1988) 394.
[5] F. Coeuret and M. Paulin, *ibid.* **18** (1988) 162.
[6] D. T. Chin, J. Y. Wang, O. Dossenbach, J. M. Locarnini and A. Numanoglu, *Electrochim. Acta.* **36** (1991) 625.
[7] J. Y. Wang, D. Balamurugan and D. T. Chin, *J. Appl. Electrochem.* **22** (1992) 240.
[8] H. Gibert and H. Angelino, *Can. J. Chem. Eng.* **31** (1973) 319.
[9] F. Coeuret and A. Stork, 'Elements de Genie Electrochimique'. Technique et Documentation (Lavoisier), Paris (1984).
[10] M. R. Mackley and X. Ni, *Chem. Eng. Sci.* **46** (1991) 3139.
[11] S. T. L. Harrison and M. R. Mackley, *ibid.* **47** (1992) 490.
[12] K. S. Rao, G. J. V. J. Raju and C. V. Rao, *Trans. Indian Inst. Chem. Engrs.* **5** (1963) 100.
[13] R. Lemlich and M. R. Levy, *Am. Inst. Chem. Engrs. J.* **7** (1961) 241.
[14] G. J. Jameson, *Chem. Eng. Sci.* **19** (1964) 793.
[15] Y. Sugano and D. A. Ratkowsky, *ibid.* **23** (1968) 707.
[16] K. M. Jolls and J. T. Hanratty, *AIChE J.* **15** (1969) 199.
[17] J. A. Karabelas, *Chem. Eng. Sci.* **26** (1971) 1581.
[18] H. Gibert, J. P. Couderc and H. Angelino, *Chem. Eng. Sci.* **27** (1972) 45.
[19] F. Coeuret, *Electrochim. Acta* **21** (1976) 185.
[20] P. N. Dwidedi and S. N. Upadhyay, *Ind. Eng. Chem, Process Des. Dev.* **16** (1977) 157.
[21] A. Gaunad and F. Coeuret, *Electrochim. Acta* **23** (1978) 1197.
[22] H. Olive and G. Lacoste, *ibid.* **24** (1979) 1109.
[23] V. G. Jenson, *Proc. Roy. Soc.* **A249** (1959) 346.
[24] F. H. Garner and R. W. Grafton, *ibid.* **A222** (1958) 64.
[25] F. H. Garner and A. H. P. Skelland, *Chem. Eng. Sci.* **4** (1955) 149.
[26] R. H. Keil and M. H. I. Baird, *Ind. Chem. Process Des. Dev.* **10** (1971) 473.
[27] R. Saint-James and G. P. Grahan, *Genie Chimie* **86** (1966) 1.
[28] O. E. Karamercan and J. L. Gainer, *Ind. Eng. Chem. Fundam.* **18** (1979) 11.
[29] D. Hersey and C. S. Im, *AIChE J.* **14** (1968) 807.