

Mass transfer at rough gas-sparged electrodes

G. H. SEDAHMED, A. Y. HOSNY*

Chemical Engineering Department, Faculty of Engineering, Alexandria University, Alexandria, Egypt

O. A. FADALLY, I. M. EL-MEKKAWY

Chemical Engineering Department, Menia University, Menia, Egypt

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Rates of mass transfer were measured by the limiting current technique at a smooth and rough inner surface of an annular gas sparged cell in the bubbly regime. Roughness was created by cutting 55° V-threads in the electrode normal to the flow. Mass transfer data at the smooth surface were correlated according to the expression

$$j = 0.126 (Fr Re)^{-0.226}$$

Surface roughness of peak to valley height ranging from 0.25 to 1.5 mm was found to have a negligible effect on the mass transfer coefficient calculated using the true electrode area. The presence of surface active agent (triton) in the solution was found to decrease the mass transfer coefficient by an amount ranging from 5% to 30% depending on triton concentration and superficial air velocity. The reduction in the mass transfer coefficient increased with surfactant concentration and decreased with increasing superficial gas velocity.

Nomenclature

a	constant	K	mass transfer coefficient (cm s^{-1})
A	electrode area (cm^2)	\bar{K}	thermal conductivity ($\text{W cm}^{-1} \text{K}^{-1}$)
C_p	specific heat capacity $\text{J g}^{-1} (\text{K}^{-1})$	V_g	superficial air velocity (cm s^{-1})
C	ferricyanide concentration (M)	Z	number of electrons involved in the reaction
d_e	annulus equivalent diameter, $(d_o - d_i)$ (cm)	Re	Reynolds number $(\rho_L V_g d_e / \mu)$
d_o	outer annulus diameter (cm)	J	mass or heat transfer J factor $(St Sc^{0.66})$ or $(St Pr^{0.66})$, respectively
d_i	inner annulus diameter (cm)	St	Stanton number $(K/V_g$ for mass transfer and $h/\rho C_p V_g$ for heat transfer)
D	diffusivity of ferricyanide ($\text{cm}^2 \text{s}^{-1}$)	Fr	Froude number $(V_g^2/d_e g)$
e	peak-to-valley height of the roughness elements (cm)	Sc	Schmidt number (ν/D)
e^+	dimensionless roughness height (e^*/ν)	Pr	Prandtl number $(C_p \mu / \bar{K})$
f	friction coefficient	ρ_L	solution density (g cm^{-3})
F	Faraday constant ($96\,500 \text{ C mol}^{-1}$)	ν	kinematic viscosity ($\text{cm}^2 \text{s}^{-1}$)
g	acceleration due to gravity (cm s^{-2})	ϵ	gas holdup
h	heat transfer coefficient ($\text{J cm}^{-2} \text{s K}$)	u^*	friction velocity $= V_L \sqrt{(f/2)}$
I_L	limiting current (A)	δ	diffusion layer thickness (cm)
		μ	solution viscosity ($\text{g cm}^{-1} \text{s}^{-1}$)

Introduction

Increasing the surface roughness of an electrode can be used to enhance the production in electrochemical reactors with diffusion controlled reactions. The use of rough electrodes has the advantage over using attached and detached inert turbulence promoters that the surface area of the electrode increases and contributes to enhancement of the rate of mass transfer along with the turbulence promotion. Although the effect of surface roughness on the rate

of mass transfer under natural convection [1], forced convection [2–7] and at gas evolving electrodes [8–11] has been studied, no previous studies have been reported on the effect of surface roughness at gas sparged electrodes. Gas sparging is gaining increasing acceptance by the electrochemical industry as a means of enhancing the rate of mass transfer in view of the fact that it consumes less power compared to mechanical stirring [12]. The use of gas sparging also allows a high residence time and a high degree of conversion in the operation of continuous electrochemi-

* Present address: College of Technology, Riyadh, Saudi Arabia.

cal reactors. The objective of the present work is to explore the possibility of using surface roughness and gas sparging together as a means of enhancing the rate of mass transfer in electrolytic cells. To this end the rate of mass transfer at the inner wall of an annular cell was determined by measuring the limiting current for the cathodic reduction of ferricyanide ion in a large excess of NaOH. Since surface active agents exist inadvertently or intentionally in solution in electrosynthesis electroplating, electroforming, and electrowinning of metals, it is of interest to study the effect of such substances on the mass transfer behaviour of gas sparged cells. The effect of surface active agents on the rate of mass transfer has been previously studied only in the case of gas evolving electrodes [13–15].

Previous studies on the effect of surface roughness on the rate of mass transfer in single phase flow [2–6] have shown that the effect of surface roughness depends on the dimensionless roughness height e^+ . For $e^+ < 3$ roughness elements are deeply submerged in the laminar sublayer and the surface behaves as a smooth surface. As e^+ increases from the smooth flow region into the transition flow region ($3 < e^+ < 25$) considerable flow separation and reattachment takes place with a marked increase in the rate of mass transfer as a result of penetration of turbulence in the valley region. As e^+ increases to the fully rough flow ($e^+ > 25$) the rate of mass transfer starts to decrease with increasing e^+ by an amount depending on Schmidt number and e^+ .

2. Experimental technique

The apparatus (Fig. 1) consisted of the cell and electrical circuit. The annular cell consisted of a vertical Plexiglass cylindrical container of 11 cm internal diameter and 60 cm height fitted with a G-3 sintered glass distributor. The inner electrode (cathode) was a nickel plated copper cylinder of 2.5 cm diameter and 30 cm height. The electrical circuit consisted of 12 V d.c. power supply with a voltage regulator and a multirange ammeter connected in series with the cell.

Before each run the cell was filled with a fresh electrolyte and air was forced through the centred glass distributor using air compressor driven by a variable speed motor. Air flow rate was determined by measuring the pressure drop across two points by means of a calibrated U-tube manometer. The limiting current for cathodic reduction of $K_3Fe(CN)_6$ was measured by increasing the current stepwise and measuring the corresponding steady state cathode potential against a reference electrode by means of a high impedance voltmeter. The reference electrode consisted of a nickel wire dipped in the cup of a Luggin tube filled with a solution identical to the cell solution; the tip of the Luggin tube was placed 0.5–1 mm from the cathode surface at its centre. The mass transfer coefficient was calculated from the

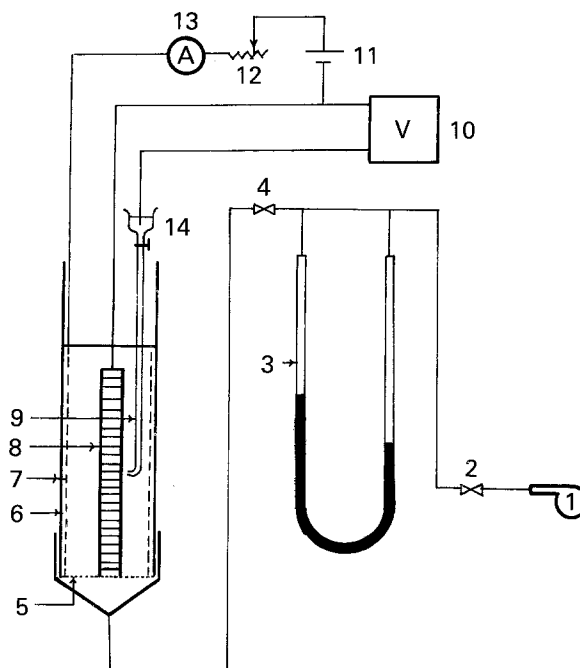


Fig. 1. Arrangement of apparatus: (1) Air compressor, (2) valve, (3) U-tube manometer, (4) valve, (5) centred glass distributor, (6) Plexiglass cell, (7) stainless steel anode, (8) nickel plated copper cathode, (9) Luggin tube, (10) voltmeter, (11) d.c. power supply, (12) variable resistance, (13) ammeter, (14) reference electrode.

limiting current using

$$K = \frac{I_L}{ZFAC} \quad (1)$$

Six rough electrodes were prepared by cutting 'V' threads in the smooth cylinder normal to the flow. The peak to valley height of the threaded electrodes were 0.25, 0.5, 0.75, 1, 1.25 and 1.5 mm. In all cases the thread angle was 55° . In calculating the mass transfer coefficient at the rough electrode the true area was used. Solutions were equimolar potassium ferricyanide and potassium ferrocyanide in 2 M NaOH. Three concentrations of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ were used, namely, 0.025, 0.05 and 0.1 M. The physical properties of the solutions used to correlate the data were obtained from the literature [16].

All experiments were conducted at $25 \pm 1^\circ C$ using freshly prepared solution. AR grade chemicals and distilled water were used. To test the effect of surfactant on the rate of mass transfer triton-X 100 ($C_{34}H_{62}O_{11}$) was added to the solution in concentration ranging from $20 \times 10^{-5} M$ to $50 \times 10^{-5} M$.

3. Results and discussions

Figure 2 shows the effect of superficial air velocity on the mass transfer coefficient in a smooth annulus. The mass transfer coefficient increases with air superficial velocity by an amount ranging from 760% to 930% compared to the natural convection value; the data fit the equation:

$$K = aV^{0.322} \quad (2)$$

The value of a depends on ferricyanide concentration which affects Sc and the saturation solubility of

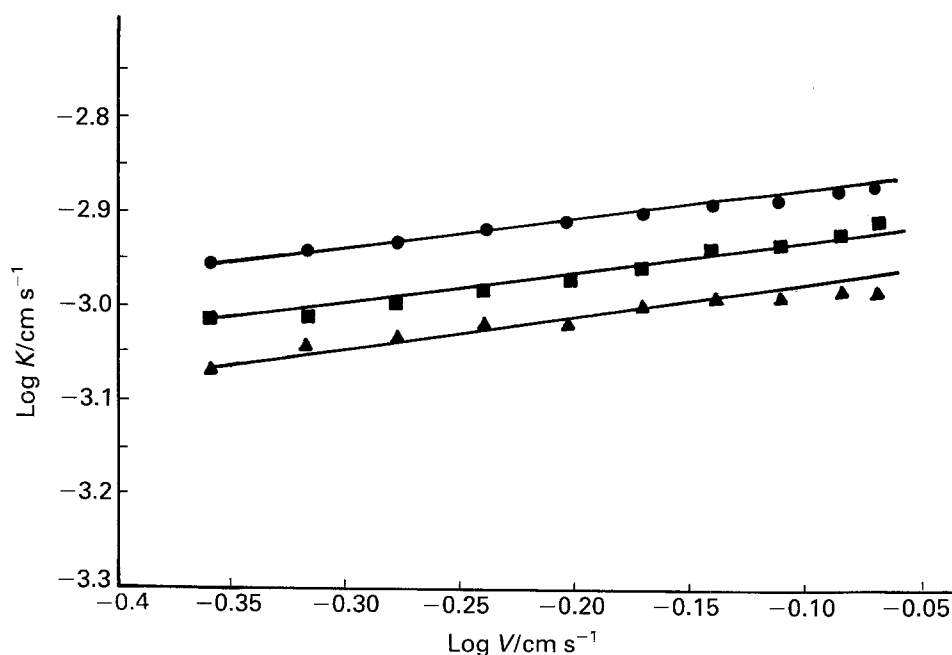


Fig. 2. Effect of superficial air velocity on the mass transfer coefficient at different ferricyanide concentration. Ferricyanide concentration: (●) 0.025; (■) 0.05; and (▲) 0.1 M.

oxygen in the solution. According to Sutey and Knudsen [17] oxygen saturation decreases the limiting current of the cathodic reduction of ferricyanide ion slightly. Under the present conditions interference from natural convection, which depends on ferricyanide concentration, is unlikely because of its small magnitude compared to convection induced by gas bubbles. The superficial velocity exponent 0.322 in Equation 2 is in agreement with the value reported by other authors who studied heat and mass transfer in bubble columns [18–29].

Based on dimensional analysis an overall mass transfer correlation was obtained using the dimensionless groups J , Fr and Re . Figure 3 shows that the data for the conditions $2043 < Sc < 2679$ and $0.0064 < Re Fr < 0.0527$ fit the equation:

$$J = 0.126 (Re Fr)^{-0.226} \quad (3)$$

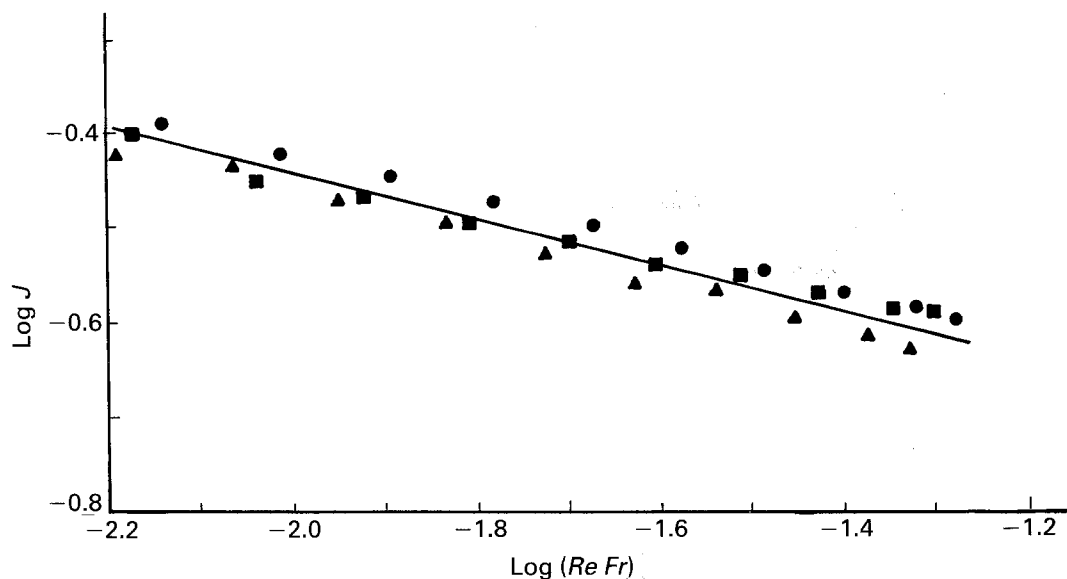


Fig. 3. Log J against log $(Re Fr)$. Ferricyanide concentration: (●) 0.25; (■) 0.05; and (▲) 0.1 M.

with an average deviation of $\pm 3.5\%$. Some previous investigators correlated their heat and mass transfer data in a manner similar to Equation 3 while others preferred, on a theoretical basis [19, 20], to use $St Sc^{0.5}$ instead of the J factor. To compare the present data with previous studies, all equations were written in terms of $St Sc^{0.5}$. Table 2 and Fig. 4 show that the present data compare favourably with those of other authors in the area of mass transfer. The discrepancy exhibited in Fig. 4 between mass transfer and heat transfer correlations may be ascribed partially to the difference between Pr and Sc ranges used in heat and mass transfer studies respectively. Most of the previous heat transfer studies were conducted using liquids of $Pr = 7$ while mass transfer studies were conducted using solutions of $Sc > 965$. Apart from the hydrodynamic effects, it is also probable that bubbles play a more active

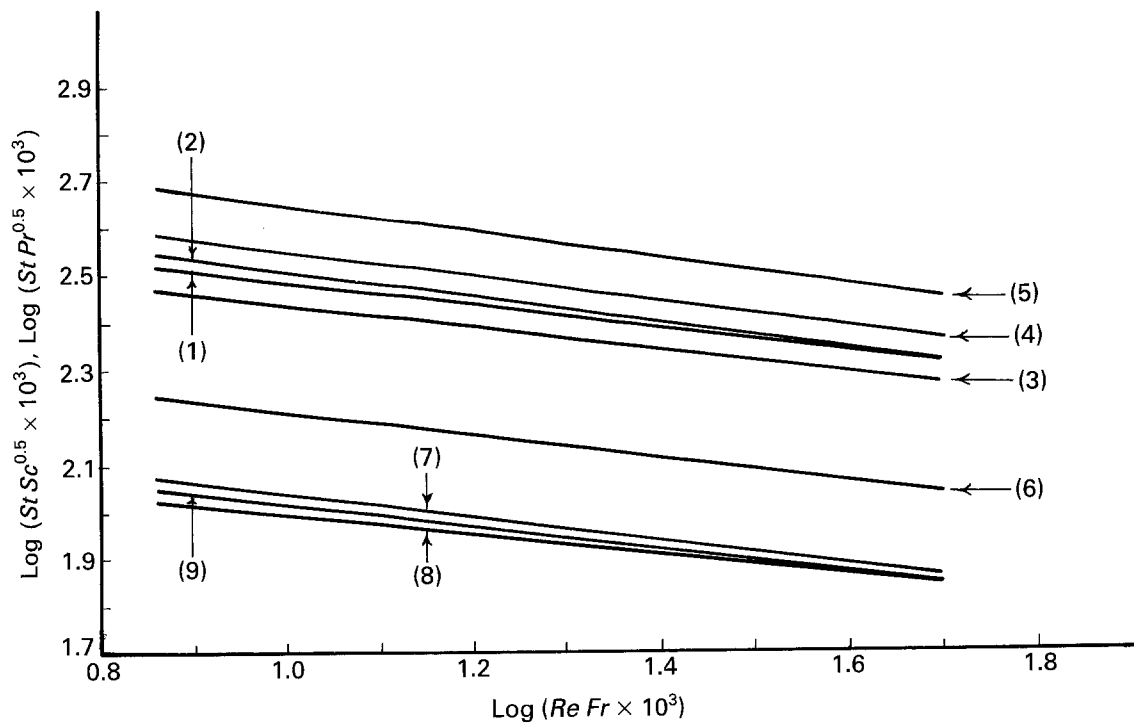


Fig. 4. Comparison of the present results with previous heat and mass transfer data. (1) Kast; (2) Hart; (3) Shaykhutdinov *et al.*; (4) Steiff; (5) Louisi; (6) Patil and Sharma; (7) Sedahmed; (8) Present work; and (9) Cavatorta and Bohm.

role in the case of heat transfer by absorbing heat from hot zones and giving it to cooler zones. The difference in pore size of the multisparger used by different authors and, therefore, bubble size was found to have a negligible effect on the mass [12] or heat [19] transfer coefficient in gas sparged systems.

Figure 5 shows the effect of thread peak-to-valley height on the mass transfer coefficient calculated using the true area of the electrode. Within the range of experimental error Fig. 5 shows that, under the present conditions, surface roughness has a negligible effect on the rate of mass transfer at gas sparged electrodes; mass transfer coefficients calculated using the projected area of the rough surface were found to be higher than the smooth surface mass transfer coefficient by an amount ranging from 12% to 47% depending on roughness height. This percentage increase in the rate of mass transfer is roughly equal to the increase in surface area due to surface roughness. The increase in the rate of mass transfer due to

surface area increase in the present case is in agreement with the fact that if the diffusion layer thickness is smaller than the roughness height, the diffusion layer follows the contours of the roughness elements with a consequent increase in the diffusional area [30, 31], under the present conditions the diffusion layer thickness ranged from 0.043 to 0.058 mm while roughness height ranged from 0.25 to 1.25 mm. Figure 5 implies that surface roughness does not enhance the rate of mass transfer at gas sparged electrodes through turbulence promotion in contradistinction to the case of single phase flow where considerable increase in the rate of mass transfer takes place. Sedahmed and Shemilt [2] who studied forced convection mass transfer at the threaded inner core of an annulus found that the rate of mass transfer increase in the turbulent flow regime was by a factor ranging from 1.125 to 4.3 depending on roughness height and Reynolds number. The authors used electrodes with peak-to-valley height ranging from

Table 1. Correlation of the data of different authors by the equation: $St Sc^{0.5} = a(Re Fr)^b$

Author	a	b	Transferent property
Kast [22]	0.112	-0.22	Heat
Hart [20]	0.103	-0.25	Heat
Deckwer [19]	0.10	-0.25	Heat (model)
Louisi [28]	0.1298	-0.27	Heat
Steiff and Weinspach [23]	0.1087	-0.26	Heat
Kolbel and Langemann [25]	0.1125	-0.22	Heat
Shaykhutdinov <i>et al.</i> [26]	0.0998	-0.22	Heat
Burkel [24]	0.096	-0.23	Heat
Cavatorta and Bohm [18]	0.0337	-0.25	Mass
Patil and Sharma [21]	0.052	-0.25	Mass
Sedahmed [29]	0.035	-0.25	Mass (model)
Present work	0.0364	-0.226	Mass

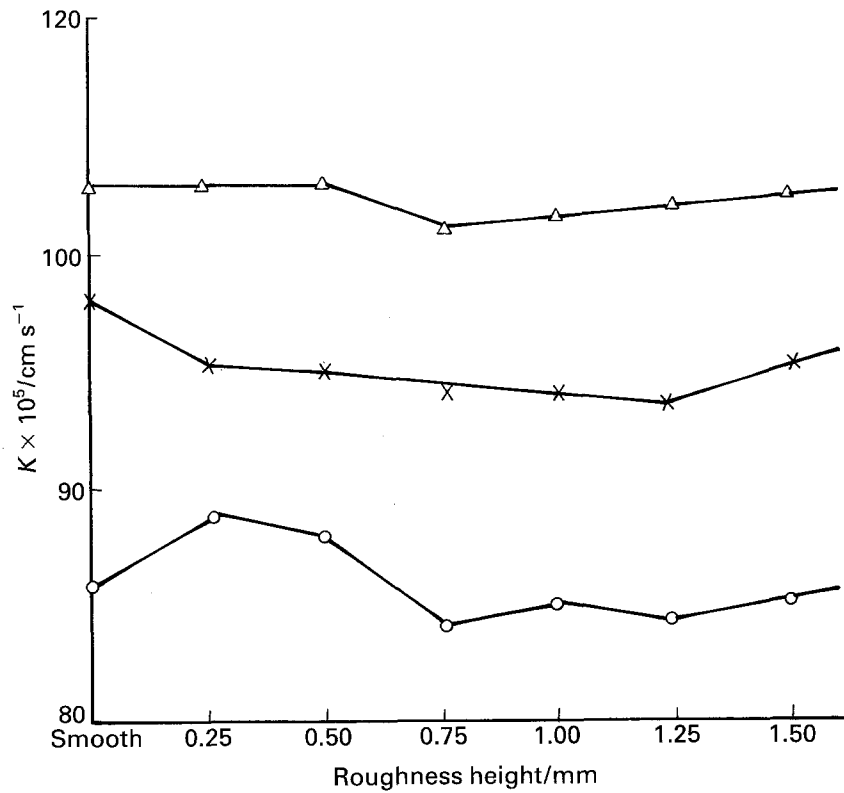


Fig. 5. Effect of Peak-to-valley height on the mass transfer coefficient at rough electrodes. Superficial air velocity: (○) 0.438; (×) 0.675; and (△) 0.849 cm s⁻¹.

0.025 to 1.648 mm and Reynolds numbers between 3700 and 30 000. The inability of surface roughness to enhance the rate of mass transfer at gas sparged electrodes may be attributed to the high mixing efficiency of the gas bubbles by virtue of their ability to generate turbulence and induce radial flow. The present finding is consistent with the finding of Economou and Alkire [32] who found that turbulence promoters have no effect on the rate of mass transfer under two phase (gas-liquid) flow in a

channel electrolyser. The present finding agrees also with the results of Sedahmed *et al.* [8] who studied the effect of surface roughness on the rate of mass transfer at gas evolving electrodes. To understand more clearly why surface roughness does not affect the rate of mass transfer at gas stirred electrodes a basic hydrodynamic study is needed to determine the nature of interaction between surface roughness and gas sparged fluids.

Figure 6 shows the effect of surface active agent

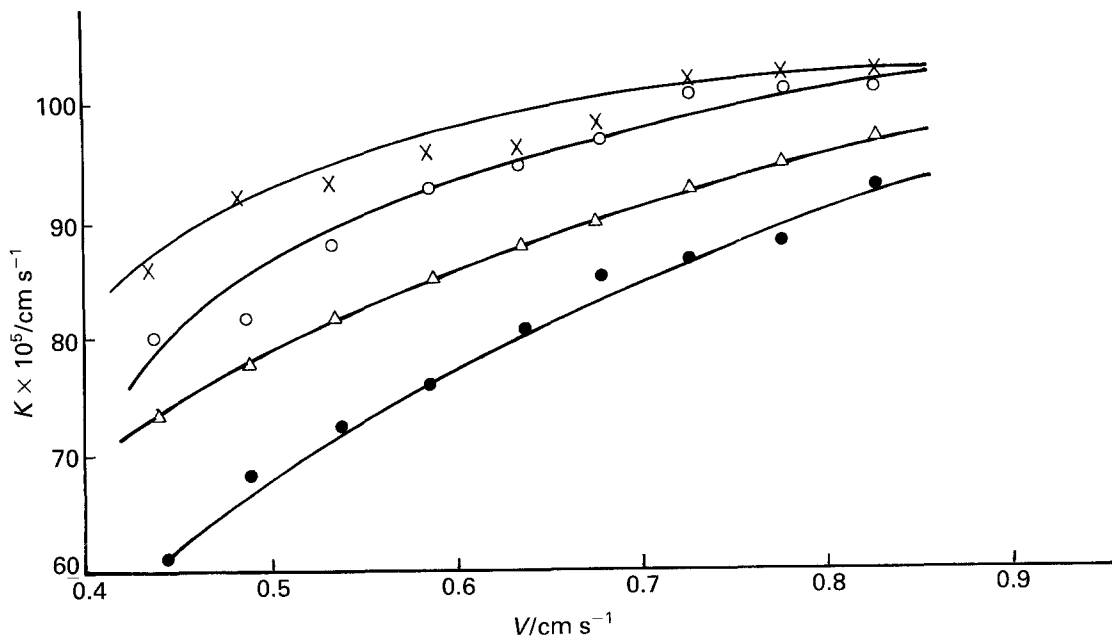


Fig. 6. Effect of superficial gas velocity on the mass transfer coefficient at different surfactant concentration. Triton concentration: (×) blank; (○) 20 × 10⁻⁵; (△) 30 × 10⁻⁵; and (●) 50 × 10⁻⁵ M.

(triton) on the mass transfer coefficient at a smooth cathode, the mass transfer coefficient decreases by an amount ranging from 5% to 30% depending on triton concentration and superficial gas velocity. This decrease in the mass transfer coefficient may be explained as follows: (i) according to Levich [33], surface active substances tend to accumulate at the interface between the bubble and the liquid and, when a bubble moves through the liquid, adsorbed surface active material is swept to the rear, creating a concentration gradient and, hence, surface tension gradient which opposes the tangential shear stress. This phenomenon increases the drag on the bubble and reduces the rise velocity; (ii) adsorption of the surfactant on the electrode surface leads to an increase in the interfacial viscosity and a corresponding decrease in the diffusivity of ferricyanide ion, this was confirmed experimentally by Ahmed and Sedahmed [13]. A comparison between the present results and the effects of surfactants on the rate of mass transfer at gas evolving electrodes [13–15] shows that the retarding effect of surfactants is less severe in the case of gas sparging because of the difference in mass transfer mechanism between the two stirring regimes. In the case of gas evolving electrodes surfactants not only affect bubble motion in solution but also lead to early bubble detachment from the electrode surface and prevent bubble coalescence on the electrode. The early disengagement of non-coalescent bubbles from the electrode surface decreases the contribution of the penetration mechanism and the microconvection mechanism [32] to the rate of mass transfer at the gas evolving electrode, while the decrease in the rise velocity of the bubbles lowers the contribution of the hydrodynamic mechanism (macroconvection) [34].

Figure 6 shows that the reduction in the mass transfer coefficient due to surfactant decreases with increasing superficial gas velocity. This may be ascribed: (i) to the increase in the number of gas bubbles passing through the solution per unit time which leads to a decreasing amount of surfactant adsorbed per bubble, with a consequent decrease in the adverse effects of the surfactant; (ii) according to Levich [33], at high bubble Reynolds number the surfactants are swept away from the bubble surface, boundary layer separation results, and the effect of

surfactants on the bubble rise velocity becomes negligible.

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