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Effect of surfactants on the rate of mass transfer at gas-evolving electrodes

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The effect of sodium lauryl sulphate surfactant on the mass transfer coefficient of the cathodic reduction of ferricyanide ion and the anode oxidation of ferrocyanide ion at hydrogen- and oxygen-evolving electrodes, respectively, was studied. Also, the effect of sodium lauryl sulphate on the gas hold-up and cell voltage was studied. The presence of surfactant in the electrolyte was found to decrease the mass transfer coefficient by an amount ranging from 7.6 to 81% depending on the operating conditions. Gas hold-up and cell voltage were found to increase in the presence of surfactant.

Nomenclature

C	concentration
F	Faraday constant (96 487 C mol^{-1})
I_L	limiting current under natural convection
I	current consumed in ferricyanide reduction or ferrocyanide oxidation during electrolysis with gas evolution
K	mass transfer coefficient
V	gas discharge rate
Z	number of electrons involved in the reaction
ε	gas hold-up

1. Introduction

In electrochemical processes surface-active substances may exist inadvertently in electrolytic solutions or may be added intentionally to the electrolyte to improve the quality of the electrodeposited metal [1]. In the case of electroorganic synthesis the reactant or one of the products may have surface activity. Sometimes surfactants are added to electrowinning solutions to control aerosol formation [2]. Although much work has been done on the effect of surfactants on liquid–gas and liquid–liquid mass transfer [3], little has been done on the effect of surfactants on mass and heat transfer in liquid–solid systems. Kar *et al.* [4, 5] studied the effect of alkyl amine surfactants on the limiting current of the cathodic reduction of oxygen on a rotating cylinder cathode. The authors found that in buffered acidic solutions surfactant has no effect on the rate of mass transfer while in unbuffered acidic solutions a decrease in the rate of mass transfer was reported owing to the deposition of a film of neutral amine molecules on the surface of the rotating cylinder cathode. Ibl and Venczel [6] studied the effect of surfactants such as gelatine and acridin on the mass transfer coefficient of the cathodic reduction of Fe^{3+} at an H_2-evolving cathode in acid solution and found that the rate of mass transfer decreased in the presence of surfactants. Morgan *et al.* [7] studied the effect of surfactants on the heat transfer coefficient during boiling and reported an increase in the rate of heat transfer in the presence of surfactant. Ahmed *et al.* [8], who studied the effect of surfactants on the neutral convection mass transfer coefficient for the electrodeposition of copper from acidified copper sulphate at vertical electrodes, reported a decrease in the rate of mass transfer.

The main object of the present work is to study the effect of surfactants, namely, sodium lauryl sulphate (SLS) on the rate of mass transfer at gas-evolving electrodes. To this end the cathodic reduction of ferricyanide and the anodic oxidation of ferrocyanide at nickel electrodes from alkaline solution were chosen. To assist in understanding the mechanism by which surfactant affects the rate of mass transfer at gas-evolving electrodes, the rate of mass transfer under natural convection was also studied. To further assist in evaluating the effect of surfactants on the performance of electrochemical reactors, the effect of sodium lauryl sulphate on gas hold-up and cell voltage was also studied.

2. Experimental details

The apparatus (Fig. 1a) consisted of a cell and electrical circuit. The cell was made of a 2-l glass container of 14-cm diameter divided into two compartments by a porous ceramic diaphragm of 7-cm diameter. The working electrode, which was placed in the inner compartment, was a nickel cylinder of 3-cm diameter and 7.7-cm height. The counter electrode was made of a cylindrical stainless steel sheet of 10-cm diameter. The electrical circuit consisted of a 6-V d.c. power supply with a voltage regulator and a multirange ammeter connected in series with the cell. Figure 1b shows the

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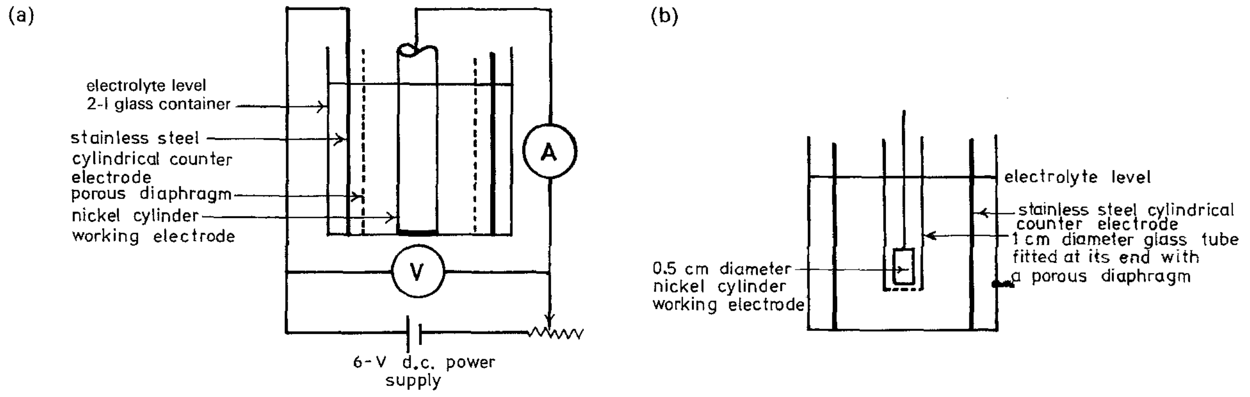

Fig. 1. (a) Cell and electrical circuit. (b) Cell used for measuring gas hold-up.

cell used in measuring the gas hold-up; the inner compartment of the cell was a 1-cm diameter glass tube fitted at its bottom with a porous diaphragm made of a synthetic fabric. The working electrode which was placed in the inner compartment consisted of a 0.5-cm diameter nickel cylinder of 2.5-cm height. The counter electrode was a 10-cm diameter cylindrical stainless steel sheet placed in a 2-l glass container. The flat bottom of the cylinder electrodes used in cells 1a and 1b was isolated with epoxy resin. The limiting current of the cathodic reduction of potassium ferricyanide and the anodic oxidation of potassium ferrocyanide was measured by increasing the current stepwise and measuring the steady state potential of the working electrode against a reference electrode by means of a high impedance potentiometer. The reference electrode consisted of a nickel wire placed in the cup of a Luggin tube filled with the cell solution; the tip of the Luggin tube was placed 0.5–1 mm from the surface of the working electrode. The mass transfer coefficient under natural convection was calculated from the limiting current using the equation

$$K = \frac{I_L}{ZFC} \qquad (1)$$

Electrolysis for measuring the effect of gas evolution on the rate of mass transfer was conducted galvanostatically using the cell shown in Fig. 1a. At the end of electrolysis the solution was analysed for ferricyanide and ferrocyanide using iodometry and permanganate titration, respectively [9]. The change in ferricyanide and ferrocyanide concentration during electrolysis under different conditions ranged from 2 to 7%. The mass transfer coefficient was calculated from the equation

$$K = \frac{I}{ZFC} \qquad (2)$$

The current I consumed in oxidizing ferrocyanide or reducing ferricyanide was calculated from the analytically determined amount reacted according to Faraday's law. The gas evolution rate was calculated from the current consumed in gas evolution using Faraday's law and the gas law. The current consumed in gas evolution is the difference between the total current passing during electrolysis and the current consumed in oxidizing or reducing ferrocyanide and ferricyanide, respectively.

The blank solution consisted of 0.1 M potassium ferri-

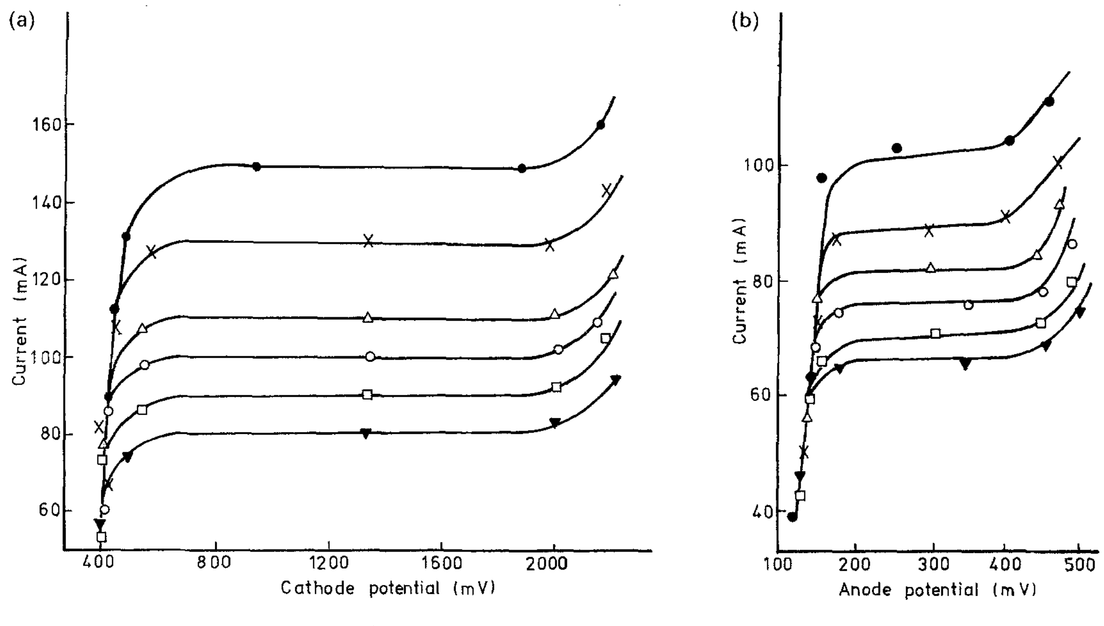

Fig. 2. Effect of surfactant concentration on the limiting current of (a) the cathodic reduction and (b) the anodic oxidation of ferricyanide ion under natural convection. Surfactant concentration $\times 10^5$ M: ● blank solution; × 7.9; △ 15.86; ○ 23.79; □ 31.72; ▼ 42.

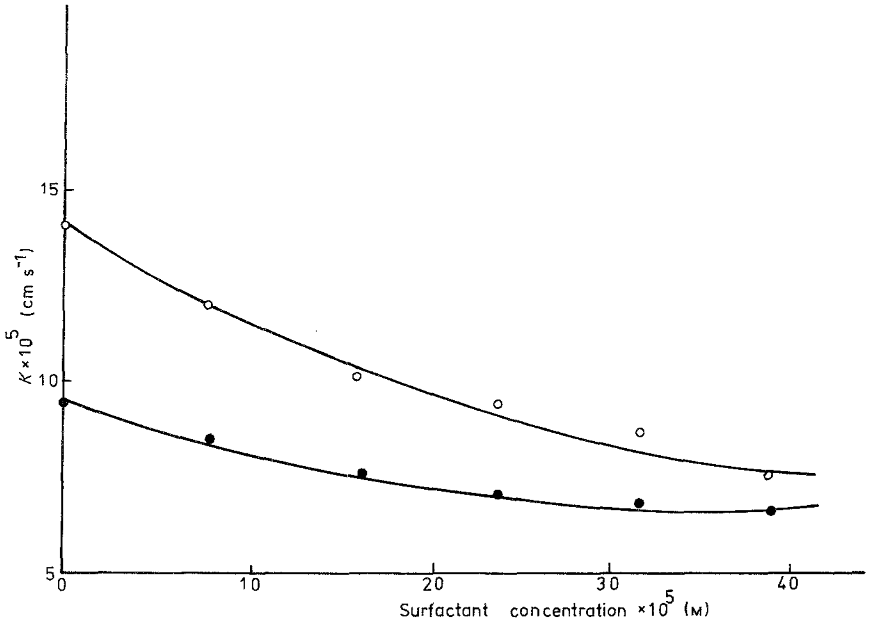

Fig. 3. Effect of surfactant concentration on the natural convection mass transfer. ○ Cathodic reduction of ferricyanide; ● anodic oxidation of ferricyanide.

cyanide, 0.1 M potassium ferrocyanide and 2 M sodium hydroxide. Sodium lauryl sulphate ($C_{12}H_{25}OS_4Na$) was added in concentrations ranging from 7.9×10^{-5} to 42×10^{-5} M. All solutions were prepared from A.R. grade chemicals and distilled water. The temperature was 15 ± 1°C. Gas hold-up (ε) was calculated from the equation

$$\varepsilon = \frac{\Delta h}{h_0 + \Delta h} \quad (3)$$

where h_0 is the height of the solution in the cell of Fig. 1b before electrolysis and Δh is the increase in solution height due to gas bubbles. The surface tension of the solution was measured before and after electrolysis by the torsion balance method [10]. The value of surface tension was the same before and after electrolysis, denoting that the surfactant did not undergo any chemical change due to electrolysis. The effect of surfactant on the diffusivity of the electroactive ion was studied by the rotating disc technique [11].

3. Results and discussion

Figures 2a and 2b show the effect of surfactant con-

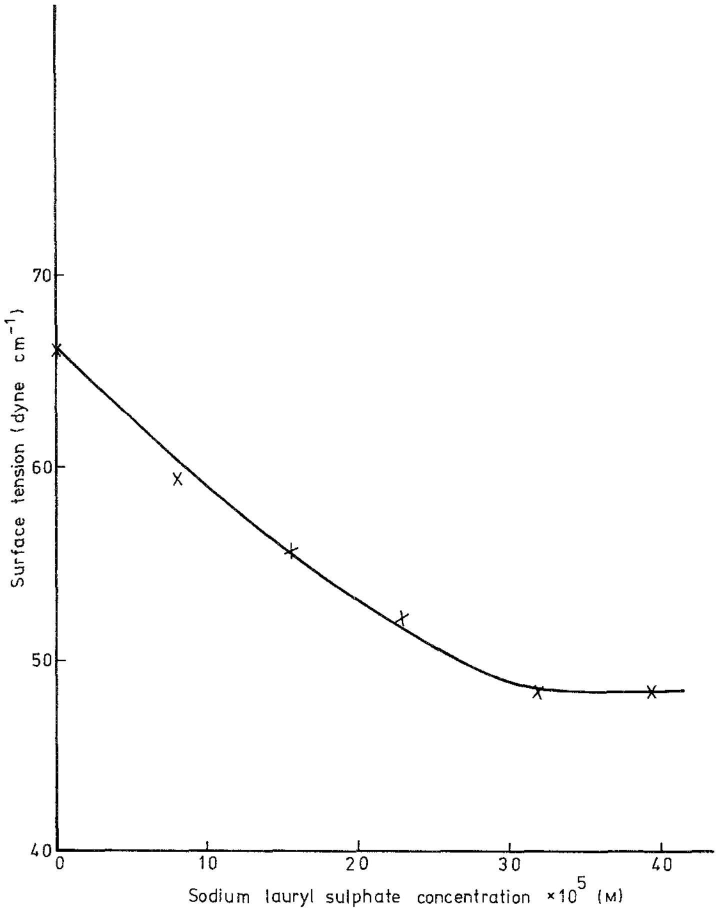

Fig. 4. Effect of surfactant concentration on solution surface tension. Blank solution: 0.1 M $K_3Fe(CN)_6$, 0.1 M $K_4Fe(CN)_6$, 2 M NaOH.

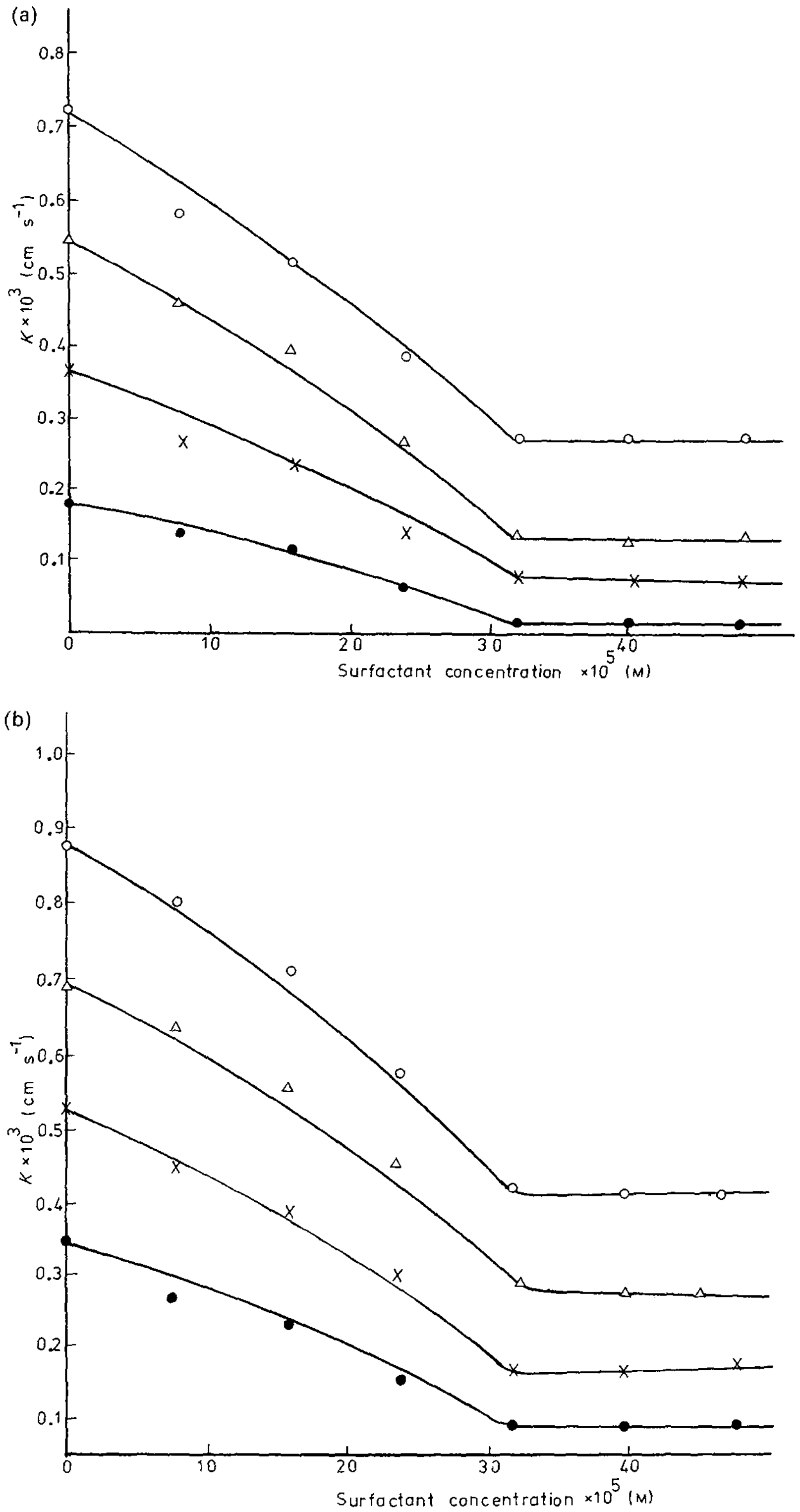

Fig. 5. (a) Effect of surfactant concentration on the mass transfer coefficient at H_2-evolving electrode. H_2 discharge rate $\times 10^3$ cm s^{-1}: ● 0.26; × 0.53; △ 0.795; ○ 1.06. (b) Effect of surfactant concentration on the mass transfer coefficient at O_2-evolving electrode. O_2 discharge rate $\times 10^3$ cm s^{-1}: ● 0.015; × 0.147; △ 0.28; ○ 0.41.

centration on the limiting current of the cathodic reduction of ferrocyanide and anodic oxidation of ferrocyanide, respectively, under natural convection. The limiting current and the mass transfer coefficient (Fig. 3) decrease with increasing surfactant concentration by an amount ranging from 13.3 to 46.8% in the case of the cathodic reduction of ferricyanide ion and by 10–30% in case of the anode oxidation of ferrocyanide ion. This decrease in the limiting current may be attributed to surfactant adsorption on the electrode surface. Concentration of the surfactant molecules at the electrode–solution interface may increase the interfacial viscosity [11] with a consequent decrease in the diffusivity of electroactive ion. Measurement of the diffusivity of ferricyanide and ferrocyanide ions in the presence of SLS by the rotating disc technique has shown that within the present range of SLS concentration the effective diffusivity of the electroactive ion decreases by an amount ranging from 5.7 to 15%. Besides, the increase in interfacial viscosity and the anchorage of the solution to the electrode surface by surfactant molecules hinder the flow of the solution past the electrode surface with a consequent decrease in the limiting current.

Figures 5a and 5b show that the mass transfer coefficient at H_2- and O_2-evolving electrodes decreases

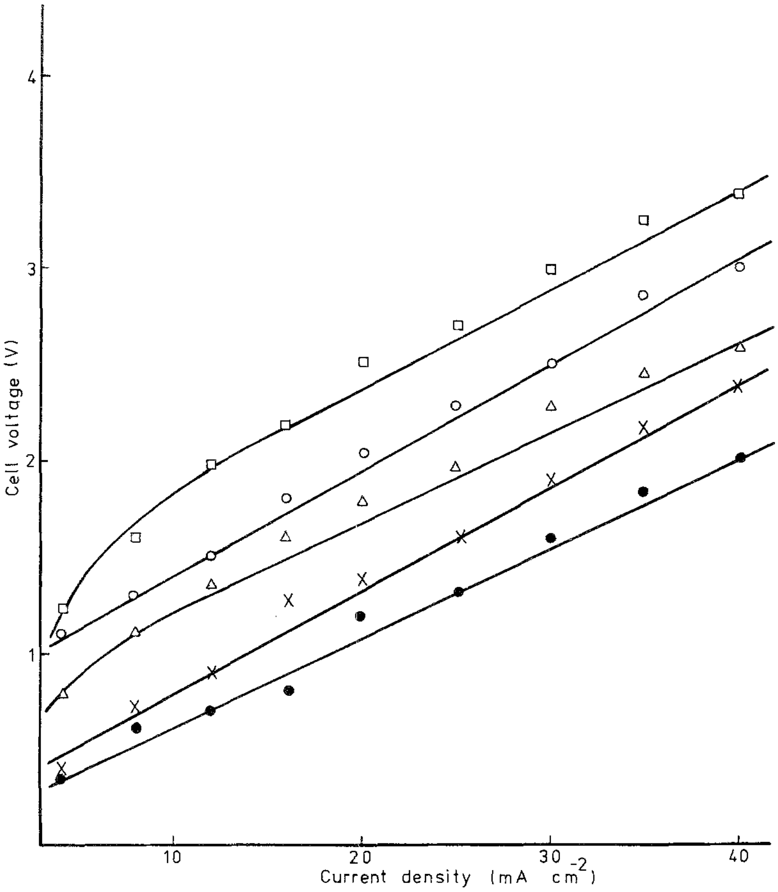

Fig. 6. Cell voltage vs current density for O_2-evolving electrode at different surfactant concentration ($\times 10^5$ M): ● blank solution; x 7.93; △ 15.86; ○ 23.79; □ 31.79.

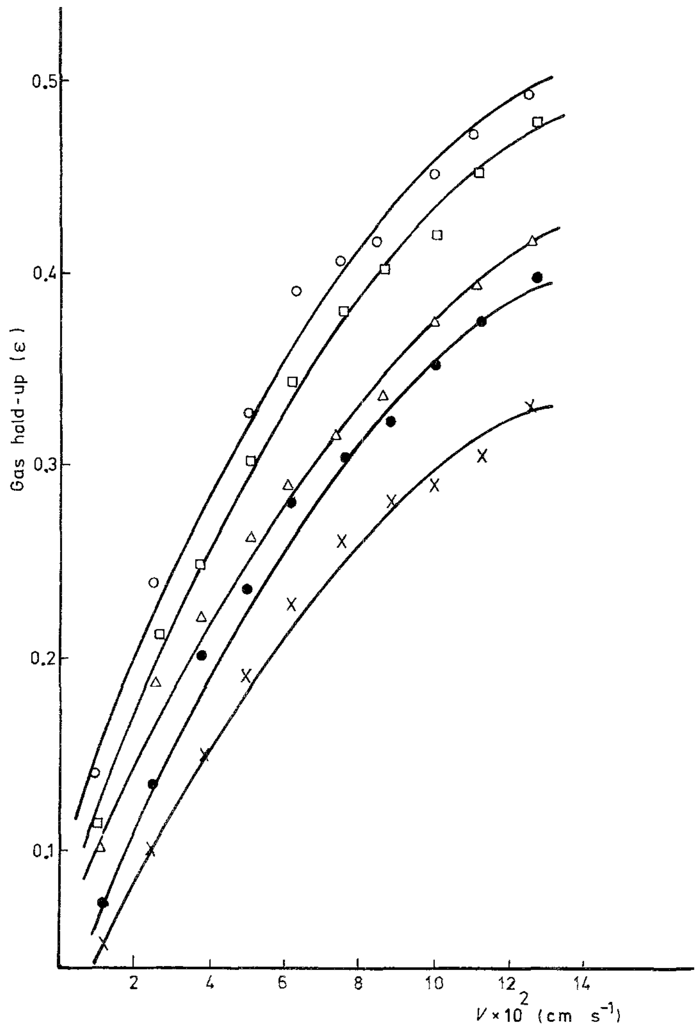

Fig. 7. Effect of oxygen discharge rate on the gas hold-up. Surfactant concentration ($\times 10^5$ M): x blank solution; ● 7.93; △ 15.86; □ 23.79; ○ 31.72.

with increasing surfactant concentration. In the case of the H_2-evolving electrode the decrease ranges from 7.6 to 75.5% while in the case of the O_2-evolving electrode the decrease ranges from 11.4 to 81%. It is well known that the presence of surfactants in solutions leads to the generation of small non-coalescent bubbles of rigid surface and of low rise velocity [3, 13, 14]. According to the penetration model [6] and the microconvection model [15] the rate of mass transfer should decrease in the presence of surfactants as a result of the early datachment of small gas bubbles from the electrode surface. Also according to the hydrodynamic model [16] and the surface renewal model [17] which depend on bubble motion in the electrolyte after datachment from the electrode surface, the rate of mass transfer should decrease in view of the low kinetic energy of the bubbles. Besides, the inability of bubbles to coalesce in the presence of surfactants reduces considerably the rate of mass transfer, especially in the case of O_2-evolving electrode where coalescence in alkaline solution is highly favoured in the absence of surfactants [16, 18]. In addition, the effects responsible for decreasing the rate of mass transfer in the case of natural convection may still be operative for gas-evolving electrodes. Figures 5a and 5b show that the mass transfer coefficient remains constant beyond a surfactant concentration of about 32.5×10^{-5} M; it seems that this concentration coincides with the critical micelle concentration (CMC) beyond which the surface tension does not change with increasing surfactant concentration as shown in Fig. 5.

Figure 6 shows the effect of surfactant on the current–cell voltage relation for the anodic oxidation of ferrocyanide with simultaneous O_2 evolution. For a given current density the cell voltage increases with surfactant concentration probably because of the increase in gas hold-up as shown in Fig. 7; gas hold-up increases the ohmic potential drop in the cell [19, 20]. The increase in gas hold-up in the presence of the surfactant may be accounted for by the decrease in bubble size and rise velocity and the difficulty of bubble escape from the rigid solution–air interface where surfactant molecules concentrate themselves with their hydrophobic radical directed to air and polar ends directed to the solution [13, 14].

In the light of the present results, the merits of surfactants should be weighed against their disadvantages before using them in diffusion-controlled electrochemical processes accompanied by gas evolution.

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