Mass transfer between rough surfaces and solutions containing drag-reducing polymers

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Rates of electrochemical mass transfer were measured between finned rotating cylinders and solutions containing drag-reducing polymers. Variables studied were: Reynolds number, polymer concentration and fin height. Polyox and carboxymethyl cellulose (CMC) were used as drag-reducing polymers with concentrations ranging from 10–100 ppm for polyox and from 10–500 ppm for CMC. Cylinders with longitudinal fins of e/d ranging from 0·0185–0·075 were used. Reynolds number was varied between 1000–10 000. It was found that the presence of fins on the cylinder surface reduces the adverse effect of the polymer on the rate of mass transfer, the higher the fin height the lower is the ability of the polymer to reduce the rate of mass transfer. Mass transfer data for solutions containing polyox were correlated by the equation:

$$(St) = 0·765 \, (Re)^{-0·36} (Sc)^{-0·669} (e/d)^{0·36}$$

Mass transfer data for solutions containing CMC were correlated by the equation:

$$(St) = 1·704 \, (Re)^{-0·36} (Sc)^{-0·75} (e/d)^{0·315}$$

List of symbols

I_L limiting current density based on the projected area of the electrode ($A \, cm^{-2}$)

K mass transfer coefficient ($cm \, s^{-1}$)

Z number of electrons involved in the electrode reaction

C ferricyanide concentration ($mol \, cm^{-3}$)

F Faraday's constant

u dynamic viscosity ($g \, cm^{-1} \, s^{-1}$)

ρ solution density ($g \, cm^{-3}$)

ω angular velocity ($rad \, s^{-1}$)

V peripheral velocity ($cm \, s^{-1}$)

D diffusion coefficient of ferricyanide ion ($cm^2 \, s^{-1}$)

d cylinder diameter (cm)

e fin height (cm)

$(Sc) = u/(\rho D)$, Schmidt number

$(Re) = \rho v d/u$, Reynolds number

$(St) = K/V$, Stanton number

1. Introduction

Some of the most important features of recent technology concern the attempt to reduce energy consumption in order to conserve the limited supply of energy available to man. A useful tool for saving power in processes involving turbulent transport of fluids is the use of drag-reducing additives which gives rise to a considerable reduction in friction with a parallel decrease in the pumping costs. The theory and mechanism of the action of drag-reducing additives are discussed elsewhere [1]. While drag-reducing additives affect beneficially the rate of momentum transfer, they adversely affect the rate of heat and mass transfer. Some work has been done to determine the extent to which rates of mass transfer are decreased in drag-reducing solutions [2–11]. So far, only smooth transfer surfaces have been used in the study of mass transfer in drag-reducing fluids.

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Rough transfer surfaces are frequently encountered in practice, and in electrochemistry, surface roughness has been suggested as a means of enhancing the rate of mass transfer for diffusion-controlled reactions [12, 13]. Additionally, surface roughness may develop during the electrochemical reaction, for instance in the electrodeposition of metals or in electrochemical machining. The aim of the present work is to study the combined effect of surface roughness and drag-reducing additives on the rate of mass transfer in diffusion-controlled electrochemical reactions, this would assist in assessing the feasibility of applying drag-reducing agents to diffusion-controlled electrochemical processes conducted under turbulent flow conditions.

2. Experimental technique

The cell used consisted of two concentric cylinders made of nickel-plated copper and placed in a one litre cylindrical glass container. The outer cylinder which had a diameter of 1 cm and an active height 12 cm was the anode. The inner cylinder which had a diameter, d, of 1 cm and an active height of 9 cm served as a rotating cathode. The cathode was driven by a variable speed motor which gave a maximum speed of 2000 rev min^{-1} without vibration or eccentric rotation. An electronic tachometer was used to measure the speed of rotation. Six cathodes were used in the study, one smooth and five rough. Roughness was made by cutting longitudinal rectangular grooves in the cylinder. The roughness elements had peak-to-valley height (e) of 0·0185, 0·026, 0·053, 0·059 and 0·075 cm giving e/d ratios of 0·0185, 0·026 0·053, 0·059 and 0·075, respectively. In all cases about 28 grooves were cut in each cylinder, the groove width being 0·5 mm. The electrical circuit used consisted of a 6 V d.c. power supply with a voltage regulator, a multi-range ammeter and the cell.

The limiting current of the cathodic reduction of $K_3 Fe(CN)_6$ was determined from polarization data which was obtained by increasing step-wise the applied potential and measuring the steady-state cathode potential against a reference electrode composed of a nickel wire placed in the cup of a Luggin tube filled with the same solution as that in the cell; the tip of the capillary end of

the Luggin tube was placed 0·5–1 mm from the rotating cylinder. The potential difference between the cathode and the reference electrode was measured by a high impedence voltmeter. The mass transfer coefficient was calculated from the limiting current using the equation:

$$I_L/ZF = KC.$$

Two polymers were used in the present study, polyethylene oxide (polyox WSR 301), a product of the Union Carbide Chemical Co., and carboxymethyl cellulose (CMC, 7H) a product of Hercules Powder Corporation. In view of the limited solubility of polyox in the electrolyte used, only three concentrations were used: 10, 50 and 100 ppm. Five concentrations of CMC were used: 10, 50, 100, 200 and 500 ppm. In all cases the electrolyte also contained:

$$0.025 \text{ M } K_3 Fe(CN)_6 + 0.025 \text{ M } K_4 Fe(CN)_6$$

$$+ 1 \text{ M NaOH}.$$
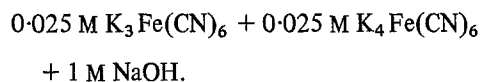
The viscosity and density of the solutions were measured by Ostwald's viscometer and a density bottle, respectively. The diffusivity of $K_3 Fe(CN)_6$ in different solutions was determined using the rotating disc technique [14].

Before each run, dissolved oxygen was removed by bubbling nitrogen gas through the electrolyte. Cathodes were degreased with trichloroethylene, then washed with alcohol and distilled water. The flat end of the cathode was insulated by polystyrene lacquer.

3. Results and discussions

Figs. 1 and 2 show the dependence of the mass transfer coefficient on the degree of surface roughness (e/d) for solutions containing polyox, and CMC of different concentrations. The mass transfer coefficient increases with increasing e/d in both polymer-free and polymer-containing solutions. Figs. 3 and 4 show that the ability of the polymer to reduce the mass transfer coefficient decreases with increasing e/d and is independent of (Re). The present finding that surface roughness reduces the effectiveness of drag-reducing polymers is in agreement with that of other authors who studied the effect of surface roughness on heat and momentum transfer to drag-reducing
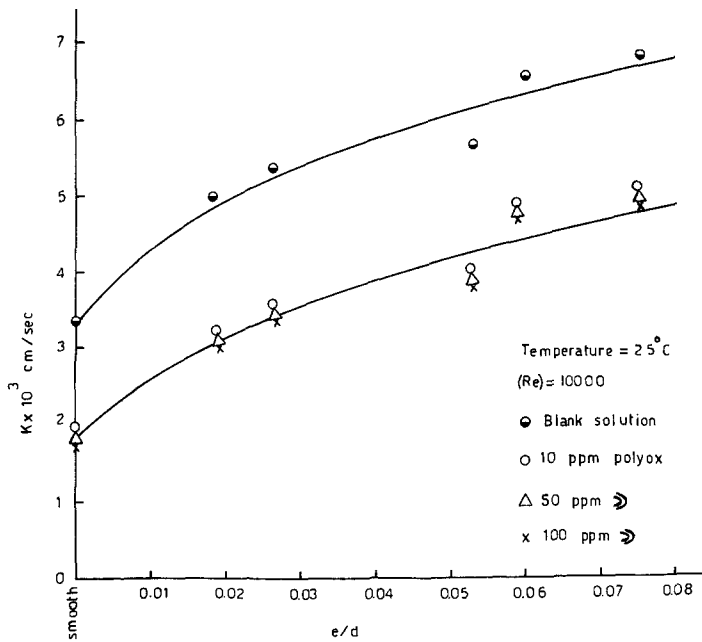
Fig. 1. Effect of e/d on the mass transfer coefficient for different polyox concentrations.

fluids using different geometries of transfer surface [15–20].

The decrease in the effectiveness of the drag-reducing polymer at rough surface was ascribed by Debrule and Saberesky [15] to mechanical degradation of the polymer caused by the high shear stress at the rough wall. However Spangler [17] showed that the loss of effectiveness was not due to polymer degradation since the friction was reduced in smooth pipe sections both upstream and downstream of the roughened area.

The decrease in polymer effectiveness at rough surfaces may, however, be explained in terms of the effect of the polymer on the turbulence structure.

Drag-reducing polymers damp only small-scale high frequency eddies [21–25] which prevail outside the laminar sub-layer of the turbulent
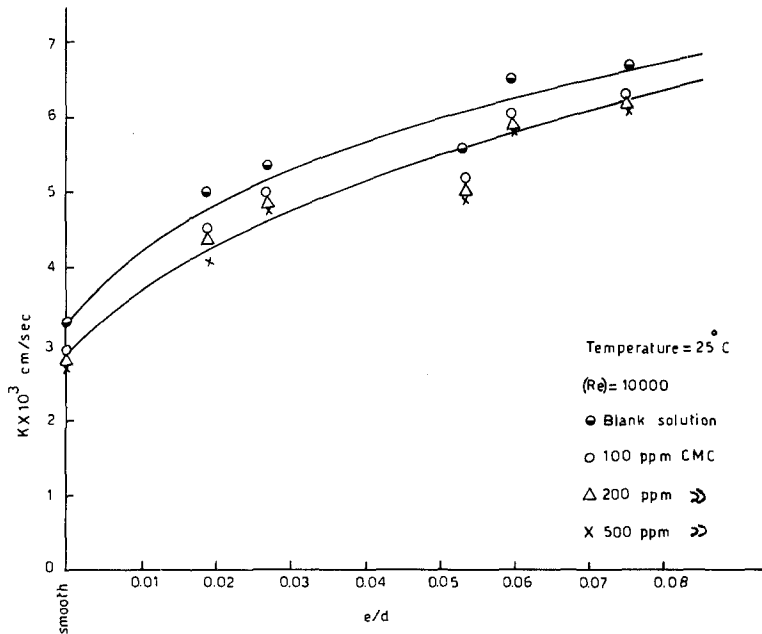

Fig. 2. Effect of e/d on the mass transfer coefficient for different CMC concentrations.
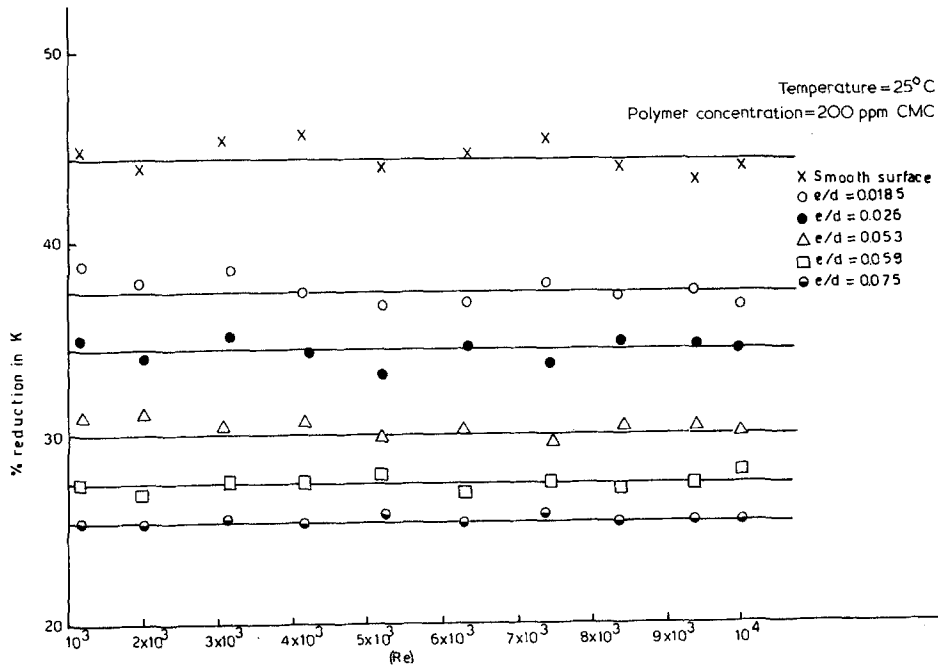
Fig. 3. Percentage reduction in K versus (Re) for solutions containing polyox at electrodes of different degrees of roughness.
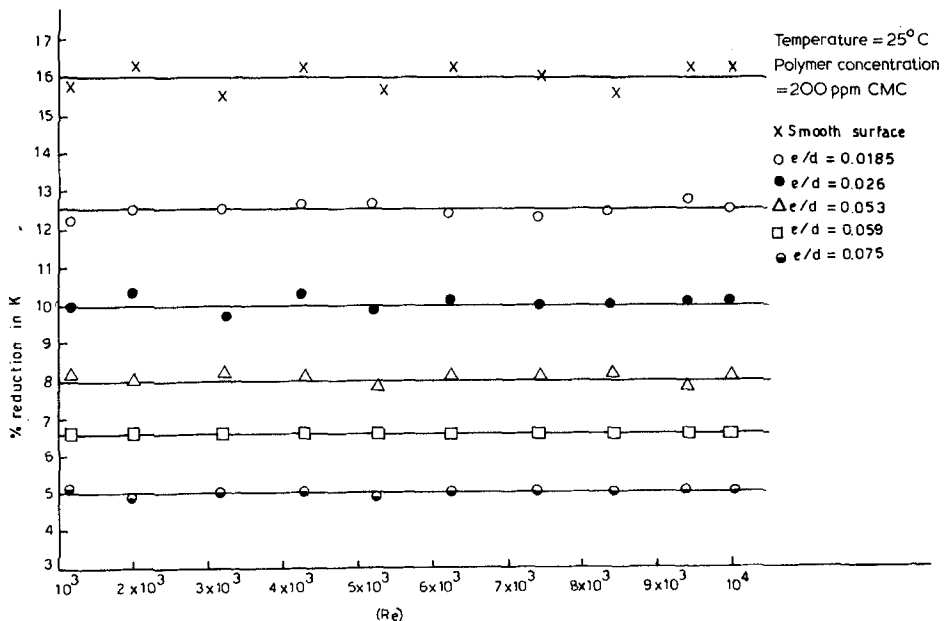

Fig. 4. Percentage reduction in K versus (Re) for solutions containing CMC at electrodes of different degrees of roughness.
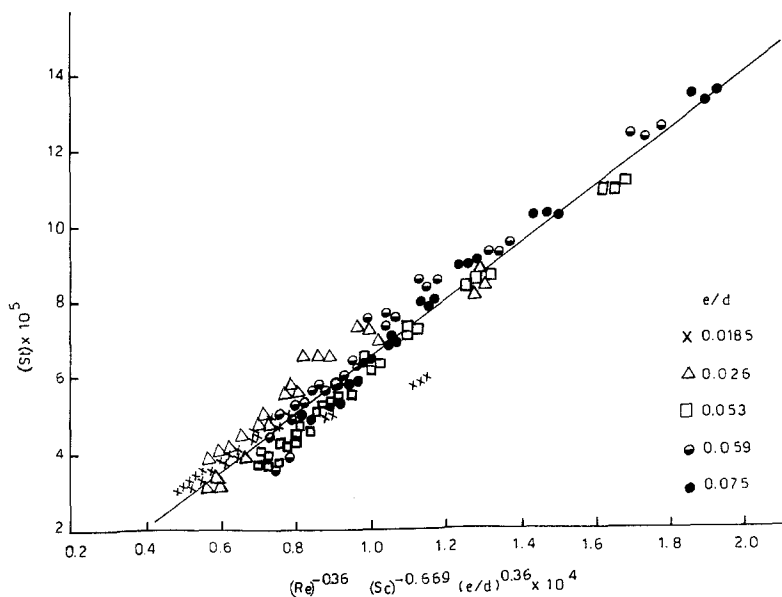
Fig. 5. Overall mass transfer correlation for solutions containing polyox at electrodes of different degrees of roughness.

hydrodynamic boundary layer. The presence of roughness elements extending outside the laminar sub-layer gives rise to boundary layer separation and the formation of eddies of different scales and different frequencies [14]. Of these eddies only the small-scale high frequency eddies are damped by the polymer molecules while the large-

scale eddies remain unaffected [25] and penetrate the laminar sub-layer leading to an enhancement in the rate of mass transfer. This compensates for the adverse effect of the polymer molecules. In the present case where surface roughness is in the form of longitudinal fins, large vortices are formed in the fin space [26–29].
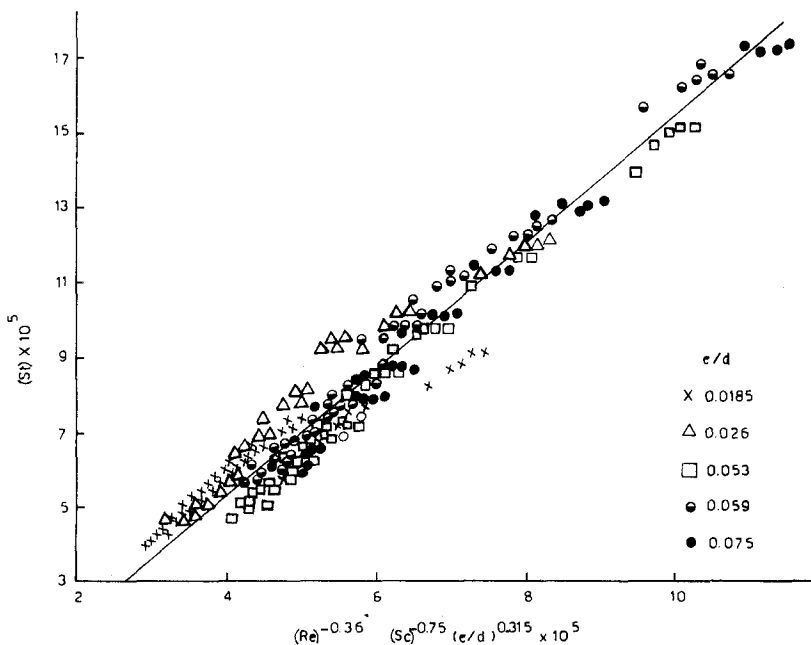

Fig. 6. Overall mass transfer correlation for solutions containing CMC at electrodes of different degrees of roughness.

These vortices escape the damping effect of polymer molecules by virtue of their size and enhance the rate of mass transfer in the fin space. In conclusion, it can be said that surface roughness and drag-reducing additives act in opposite directions on the rate of mass transfer. While drag-reducing additives tend to decrease the rate of mass transfer through damping small-scale high frequency eddies, surface roughness tends to increase the rate of mass transfer through the formation of large-scale eddies. In the present study it was found that the effect of surface roughness is predominant. Mass transfer data was correlated in terms of the dimensionless groups (St), (Sc) and (Re); Fig. 5 shows that for solutions containing polyox, the data fit the following equation with an average deviation of 4·9%:

$$(St) = 0·765 (Re)^{-0·36} (Sc)^{-0·669} (e/d)^{0·36}.$$

For solutions containing CMC, the data was correlated with an average deviation of 7% by the equation:

$$(St) = 1·704 (Re)^{-0·36} (Sc)^{-0·75} (e/d)^{0·315}$$

In polymer-free solutions, mass transfer data at rotating finned cylinders was correlated by the equation [13]

$$(St) = 0·714 (Re)^{-0·39} (Sc)^{-0·644} (e/d)^{0·2}$$

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