Effect of drag-reducing additives on the rate of mass transfer in diffusion-controlled electrochemical processes

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Mass transfer between a rotating cylinder and a solution containing sodium carboxymethyl cellulose polymer, was studied using an electrochemical technique involving the reduction of potassium ferri-cyanide in a large excess of sodium hydroxide. The Reynolds number and polymer concentration were varied over the ranges 4100–41 000 and 10–500 ppm, respectively. Under these conditions, it was found that polymer addition reduces the mass transfer coefficient by 10–22% depending on Reynolds number and polymer concentration. The mass transfer data in polymer-containing solutions were found to fit the equation

\[(St) = 0.07(Re)^{-0.3}(Sc)^{-0.644}\]

List of symbols

- \(I_L\) limiting current density (A cm\(^{-2}\))
- \(Z\) number of electrons involved in the reaction
- \(F\) Faraday’s constant (96 500 C)
- \(K\) mass transfer coefficient (cm s\(^{-1}\))
- \(V\) linear velocity of the cylinder (cm s\(^{-1}\))
- \(\omega\) angular velocity (rad s\(^{-1}\))
- \(D\) diffusion coefficient (cm\(^2\) s\(^{-1}\))
- \(\nu\) kinematic viscosity (cm\(^2\) s\(^{-1}\))
- \(d\) diameter of the cylinder (cm)
- \(\mu\) viscosity of the solution (poise)
- \(\rho\) density of the solution (g cm\(^{-3}\))
- \(C\) concentration (mol cm\(^{-3}\))
- \(St = K/V\), Stanton number
- \(Sc = \nu/D\), Schmidt number
- \(Re = \rho \omega d/\mu\), Reynolds number

1. Introduction

The phenomenon of drag reduction exhibited by dilute polymer solutions is of great potential value to the electrochemical industry where many processes are conducted under turbulent-flow conditions. The application of the phenomenon to electrochemical processes would lead, under optimum conditions, to a reduction in the operating costs of these processes owing to the decrease in the pumping power requirement. However, before a final decision can be made on the application of drag-reducing polymers to electrochemical processes, some reservations should be dispelled. The two most important of these reservations are the adverse effect of the polymer on the rate of mass transfer and the compatability of the polymer with the electrolytic solutions. The performance of the polymer as a drag-reducing agent and its compatibility with electrolytic solutions depend, among other factors, on the chemical structure of the polymer. In a previous report, [1] the authors tested the effect of polyethylene oxide polymer (polyox) on the rate of mass transfer in the cathodic reduction of potassium ferricyanide at rotating cylinder electrodes. It was found that polyox reduces the rate of mass transfer by a maximum of 47%. This result motivated the authors to test the performance of polyox as a corrosion inhibitor using the anodic dissolution of copper in phosphoric acid. A reduction in the limiting current of copper dissolution up to 40% was obtained [2].

Although polyox is one of the most effective drag-reducing polymers, it has some limitations, for example, its susceptibility to mechanical
Degradation is relatively high [3]. This limits the time during which the polymer can act as a drag reducer. Also, the polymer does not dissolve in many electrolytic solutions because of the salting-out effect [4]. This represents a serious limitation if the polymer is to be applied to electrochemical processes. The present work reports on the effect of carboxymethyl cellulose sodium salt (CMC) on the rate of electrochemical mass transfer. Previous work on CMC has concentrated on its drag-reducing ability [5-10] but little has been done on its effect on heat [11] and mass transfer [12]. Although CMC is less effective as a drag-reducing agent than polyox [13], it is more resistant to mechanical degradation [3] and its solubility in alkaline and neutral electrolytic solutions is better than that of polyox [12].

To compare the results of the present work with the results of the author's previous work, the present study was undertaken under similar conditions. Limiting currents were measured for the cathodic reduction of potassium ferricyanide in a large excess of sodium hydroxide as the supporting electrolyte to prevent the transfer of ferricyanide ion to the electrode surface by electrical migration. The system is chemically compatible with CMC [14, 15]. A rotating cylinder cathode was chosen in this study for two reasons. Firstly, the mass transfer correlation of this geometry in polymer-free solution is established [16] thus providing a means to test the soundness of the present experimental technique. Secondly, as the flow at a rotating cylinder is highly turbulent, this provides the ideal condition for the polymer to exhibit its property as a drag-reducing agent.

2. Experimental technique

Fig. 1 shows the experimental set-up. The electrical circuit consisted of a 6 V d.c. power supply with a voltage regulator, a multirange ammeter and the electrolytic cell. The cell consisted of a nickel-plated copper cylinder cathode of diameter 2 cm rotating in the centre of a 10 cm internal diameter glass container holding 1000 ml of the electrolyte; the cathode was surrounded by a cylindrical sheet of nickel plated copper of diameter 10 cm acting as anode. The cathode was driven by a variable speed motor over the range 200–2000 rev min⁻¹. Special precautions were taken to eliminate