

# *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 ferricyanide 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 ( $A\text{ cm}^{-2}$ )
$Z$	number of electrons involved in the reaction
$F$	Faraday's constant (96 500 C)
$K$	mass transfer coefficient ( $\text{cm s}^{-1}$ )
$V$	linear velocity of the cylinder ( $\text{cm s}^{-1}$ )
$\omega$	angular velocity ( $\text{rad s}^{-1}$ )
$D$	diffusion coefficient ( $\text{cm}^2\text{ s}^{-1}$ )
$\nu$	kinematic viscosity ( $\text{cm}^2\text{ s}^{-1}$ )
$d$	diameter of the cylinder (cm)
$u$	viscosity of the solution (poise)
$\rho$	density of the solution ( $\text{g cm}^{-3}$ )
$C$	concentration ( $\text{mol cm}^{-3}$ )
$(St)$	$= K/V$ , Stanton number
$(Sc)$	$= \nu/D$ , Schmidt number
$(Re)$	$= \rho vd/u$ , 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 compatibility 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  $\text{rev min}^{-1}$ . Special precautions were taken to eliminate

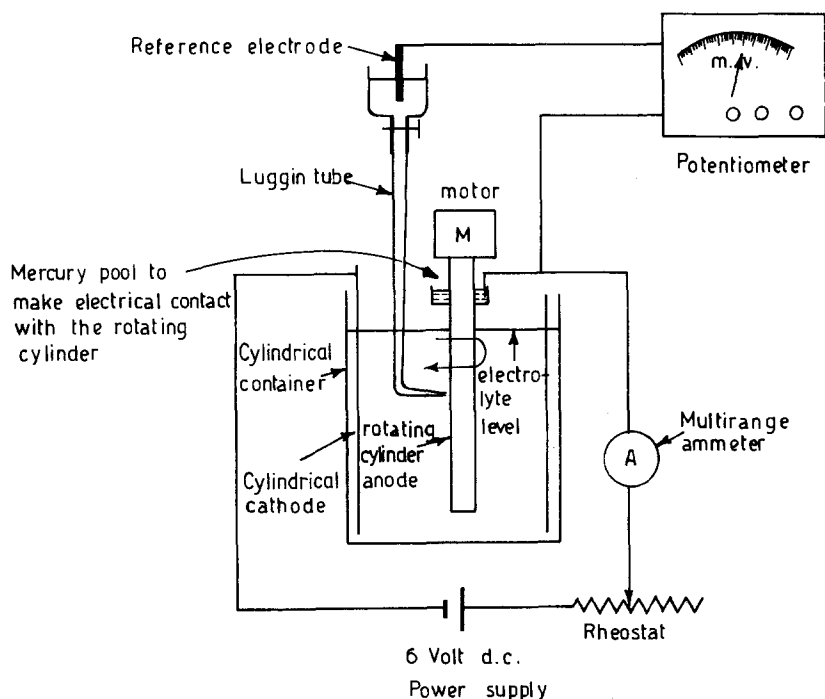
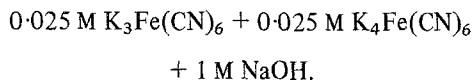


Fig. 1. Cell and electrical circuit.

vibrations and eccentric rotation. Current-potential curves were constructed by increasing stepwise the applied current and measuring the steady-state cathode potential against a reference electrode which was placed in the cup of a luggin tube filled with the same solution used in the cell. The tip of the capillary end of the luggin tube was placed 0.5–1 mm from the rotating cylinder. The limiting current was determined from the current-potential curve and used to calculate the mass transfer coefficient according to the equation

$$I_L/ZF = KC. \quad (1)$$

The CMC, 7H (a product of Hercules), of molecular weight 700 000 was used in this study. Five concentrations were used; 10, 50, 100, 200 and 500 ppm. In all cases, the electrolyte used was composed of:



The viscosity and density of the solutions were measured by Ostwald's viscometer and a density bottle, respectively. The diffusivity of  $\text{K}_3\text{Fe}(\text{CN})_6$  in different solutions was determined using the

rotating disc technique [17]. A 1.52 cm nickel-plated copper disc was rotated in the solution in the laminar flow regime, and the rate of mass transfer was determined by measuring the limiting current of the cathodic reduction of  $\text{K}_3\text{Fe}(\text{CN})_6$  at the surface of the disc. The diffusion coefficient was calculated using the Levich equation [13]

$$I_L = 0.62ZF\omega^{1/2}D^{2/3}\nu^{-1/6}C. \quad (2)$$

### 3. Results and discussion

Figs. 2a and b show a typical current-potential curve obtained with and without polymer addition using the rotating disc and the rotating cylinder, respectively. The drag-reducing properties of the polymer, namely damping of the turbulent eddies in the buffer region of the boundary layer, manifests itself by lowering the limiting current as seen in Fig. 2b. Fig. 2a shows that in the laminar flow regime, the polymer has no effect on the limiting current. Fig. 3 shows the dependence of the limiting current on the angular velocity of rotation of the disc electrode in the laminar flow regime. As seen from the figure the relation between the

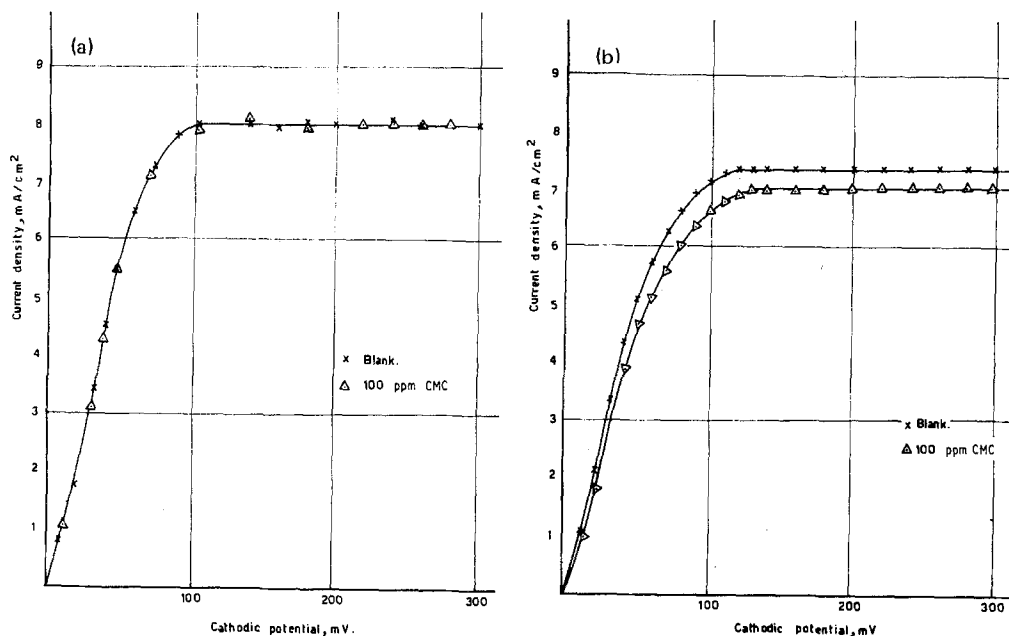


Fig. 2. (a) Effect of polymer addition on polarization of the rotating disc electrode in the laminar flow region. Disc diameter, 1.52 cm; temperature, 25°C; 600 rev min<sup>-1</sup>. (b) Effect of polymer addition on polarization of the rotating cylinder electrode in the turbulent flow regime. Cylinder diameter, 2 cm; temperature, 25°C; 1000 rev min<sup>-1</sup>.

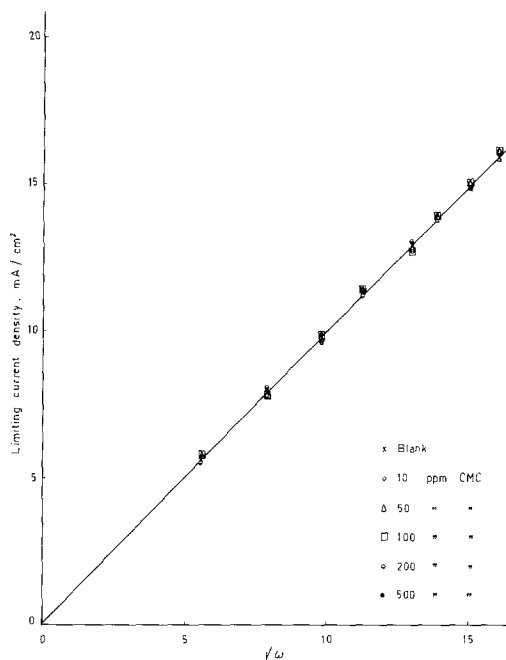


Fig. 3. Cathodic limiting current versus angular disc velocity for different concentrations of CMC.

limiting current and the square root of the angular velocity is represented by a straight line passing through the origin of the coordinates, agreeing with Levich equation [17]. This agreement testifies to the soundness of the electrochemical technique and rules out the possible disturbance which may arise from polymer adsorption on the electrode surface.

Fig. 3 also shows that CMC addition within the concentration range 10–500 ppm has no effect on the diffusivity of the ferricyanide ion.

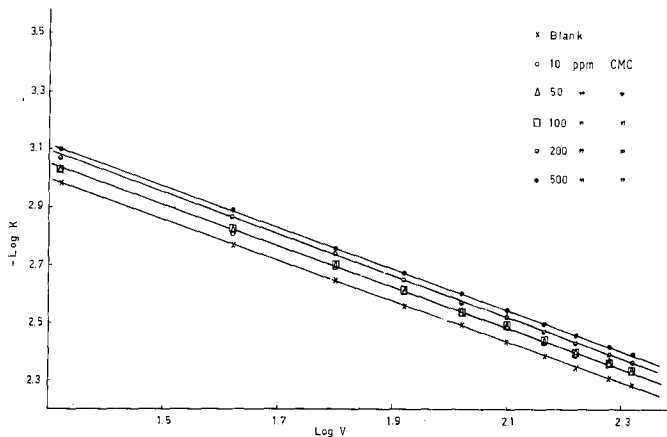


Fig. 4. Log  $K$  versus log  $V$  for different concentrations of CMC solution.

Fig. 4 shows the effect of the linear velocity of the rotating cylinder electrode under turbulent flow conditions on the mass transfer coefficient in solutions of different CMC concentrations. The data fit the relation

$$K = \text{constant } V^{0.7}. \quad (4)$$

The velocity exponent is in agreement with the value reported by Eisenberg *et al.* [16] who studied mass transfer at rotating cylinders in polymer-free solutions. An overall mass transfer correlation was envisaged in terms of the dimensionless groups:  $(St)$ ,  $(Sc)$  and  $(Re)$  as shown in Fig. 5. In polymer-free solution, the data were found to fit the equation

$$(St) = 0.079(Re)^{-0.3}(Sc)^{-0.644} \quad (5)$$

with an average deviation of 0.9%. The data are in agreement with those of Eisenberg *et al.* [16].

In solutions containing CMC, the mass transfer data were found to fit the equation

$$(St) = 0.07(Re)^{-0.3}(Sc)^{-0.644}$$

with an average deviation of 1.7%.

Table 1 shows the percentage reduction in the mass transfer coefficient at different polymer concentrations. The reduction ranges from about 9.6 to 22% depending on polymer concentration. Within the range of  $(Re)$  used in this work (4100–41 000), the percentage decrease in the mass transfer coefficient at any polymer concentration is insensitive to the value of  $(Re)$ . This phenomenon may be explained by the fact that the polymer molecules are completely stretched by virtue of the repulsion between the negatively charged

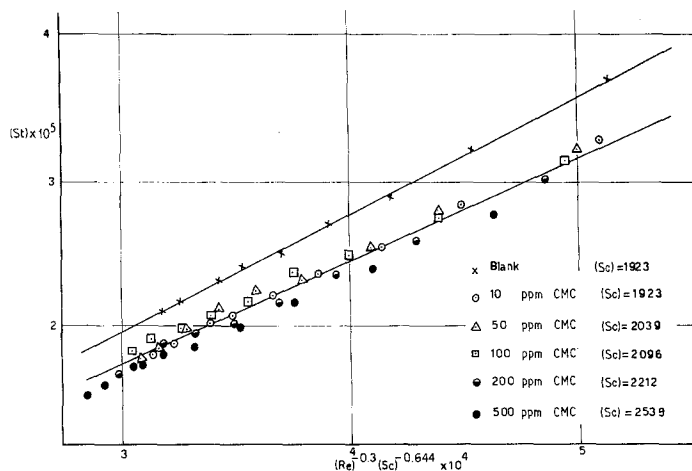


Fig. 5. Overall mass transfer correlations for solutions with and without polymers at the rotating cylinder electrode.

segments of the polymer anion. Any increase in ( $Re$ ) will not result in further stretching of the polymer molecules. Since the efficiency of the polymer as a drag-reducing agent depends on its degree of stretching [18], it follows that the effect of a fully-stretched polymer on the rate of mass transfer is independent of ( $Re$ ).

Pruitt *et al.* [11] who studied heat transfer in dilute CMC solutions using tubular geometry under turbulent flow, reported a decrease in the rate of heat transfer due to the presence of CMC. This is in agreement with the present findings.

It is obvious from the present results and the results of previous studies under similar conditions [1, 2] that the ability of CMC to reduce the rate of mass transfer is less than that of polyox. This is consistent with the fact that polyox is a more effective drag-reducing agent than CMC [13], i.e.

the ability of polyox to damp eddies in the hydrodynamic boundary layer and increase the diffusion-layer thickness is much higher than that of CMC. The superiority of polyox as a drag-reducing agent is attributed to the high flexibility of its molecules and its high molecular weight [13] compared to that of CMC.

#### Acknowledgement

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Table 1. Effect of CMC concentration on the percentage reduction in mass transfer coefficient

$(Re)$	% reduction in $K$				
	10 ppm	50 ppm	100 ppm	200 ppm	500 ppm
4183	10.52	10.52	10.52	15.80	21.04
8365	9.69	11.61	12.90	16.14	22.59
12560	9.76	10.73	12.20	17.10	21.96
16743	10.01	10.01	12.00	16.00	22.00
20925	10.17	11.86	8.47	16.95	22.03
25120	10.44	8.95	11.94	16.41	22.38
29303	10.67	9.33	11.99	16.00	21.33
33485	9.64	12.05	10.85	15.66	21.69
38058	10.12	11.23	8.99	16.86	22.48
41863	10.53	11.58	9.48	16.84	22.11

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