JOURNAL OF APPLIED ELECTROCHEMISTRY **10** (1980) 245–250

A comparative study of the effect of different drag-reducing polymers on electrochemical mass transfer

G. H. SEDAHMED, A. ABDEL-KHALIK

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

Received 12 April 1979

The effect of Polyox, Separan and CMC drag-reducing polymers on the rate of electrochemical mass transfer was studied using the cathodic reduction of $K_3Fe(CN)_6$ in neutral media at a rotating cylinder cathode. Reynolds number and polymer concentration were varied over the ranges 764–10 470 and 10–200 ppm respectively. Under these conditions it was found that the three polymers reduce the rate of mass transfer by a maximum of 47%, 30%, and 17% for Polyox, Separan and CMC, respectively. Mass transfer data in the three polymer solutions was correlated by the following equations:

for Polyox:

$$(St) = 0.051(Re)^{-0.3}(Sc)^{-0.644}(u/u_0)^{-0.7}$$

for Separan:

$$(St) = 0.065(Re)^{-0.3}(Sc)^{-0.644}(u/u_0)^{-0.7}$$

for CMC:

$$(St) = 0.075(Re)^{-0.3}(Sc)^{-0.644}(u/u_0)^{-0.5}$$

List of symbols

I	limiting current density ($A\,cm^{-2}$)
Z	number of electrons involved in the reaction
F	Faraday's constant
K	mass transfer coefficient ($cm\,s^{-1}$)
V	linear velocity of the cylinder ($cm\,s^{-1}$)
D	diffusion coefficient ($cm^2\,s^{-1}$)
ν	kinematic viscosity ($cm^2\,s^{-1}$)
d	diameter of the cylinder (cm)
u, u_0	viscosity of solutions with and without polymer respectively (P)
ρ	density ($g\,cm^{-3}$)
c	concentration of $Fe(CN)_6^{3-}$ ($mol\,cm^{-3}$)
(St)	Stanton number $= K/V$
(Sc)	Schmidt number $= \nu/D$
(Re)	Reynolds number $= \rho Vd/u$

1. Introduction

Recently the use of drag-reducing additives has been introduced to electrochemical engineering with the object of decreasing the pumping power necessary in turbulent flow electrochemical processes. In an effort to assess the feasibility of applying the phenomenon of drag reduction to electrochemical processes, work has been done on the possible adverse side effects of drag-reducing additives on the rate of mass transfer of diffusion-controlled electrochemical reactions. In this respect, two polymers have been tested, namely, CMC in alkaline medium [1], and Polyox in acid [2] and alkaline [3] media. The present work is concerned with a compartive study of the effect of the three drag-reducing polymers (CMC, Polyox and Separan) on the rate of electrochemical mass transfer. The cathodic reduction of $K_3Fe(CN)_6$ in a large excess of sodium sulphate as the supporting electrolyte at a rotating cylinder was chosen for the present study. In neutral solutions the three polymers are chemically stable and highly soluble.

2. Experimental technique

The electrical circuit consisted of a 6 V d.c. power supply with a voltage regulator, a multi-range ammeter and the cell. The cell consisted of a nickel-plated copper cylinder cathode of 2 cm diameter and 8 cm active height rotating in the centre of a glass container with an internal diameter of 10 cm. The cathode was surrounded by a cylindrical platinum wire gauze of 10 cm

0021–891X/80/020245–06$02.60/0

diameter and 10 cm height. A variable speed motor was used to drive the cathode. An electronic tachometer was used to measure the rotational speeds. Care was taken to avoid vibration and eccentric rotation.

The blank solution used in the present study was composed of:

$$0.01\ \mathrm{M}\ K_3Fe(CN)_6 + 0.01\ \mathrm{M}\ K_4Fe(CN)_6 + 0.5\ \mathrm{M}\ Na_2SO_4.$$

Three polymers were used, polyethylene oxide (Polyox WSR 301) a product of Union Carbide, polyacrylamide (Separan Ap-30) a product of Dow Chemical Co. and carboxymethyl cellulose (CMC-7H) a product of Hercules. The polymer solution was prepared by digesting the required weight of polymer in distilled water for about 24 h and then mixing with a blank solution to give the required composition. The mass transfer coefficient was obtained from the limiting current using the equation

$$K = I/(ZFC). \qquad (1)$$

The limiting current was determined from polarization curves which were constructed by increasing the applied current step-wise and measuring the steady state cathode potential against a reference electrode. The reference electrode consisted of a nickel wire dipped in the cup of a luggin tube filled with an identical solution to that in the cell, the tip of the luggin tube was placed at 0.5–1 mm from the rotating cylinder. Polymer concentrations ranged from 0–200 ppm; all solutions were found to be Newtonian [4–8]. The viscosity and density of the solutions were determined using an Ostwald viscometer and a density bottle, respectively. The diffusion coefficient of ferricyanide ion in different solutions was determined by the rotating disc technique [9].

3. Results and discussions

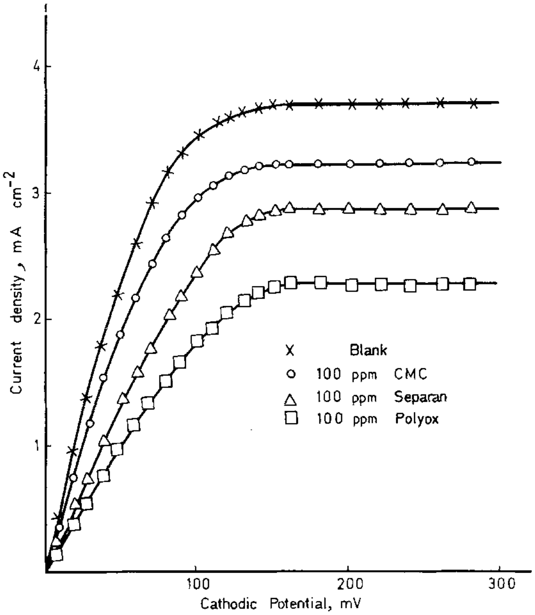

Fig. 1. Effect of different polymer solutions on polarization of the rotating cylinder electrode in turbulent flow regime. Cylinder diameter 1 cm, temperature 25° C, 2000 rev min^{-1}.

Figs. 1 and 2 and Table 1 show a comparison of the effect of the three polymers on the limiting current and the mass transfer coefficient; Polyox is the most effective mass transfer reducer followed by Separan and CMC, respectively. This is consistent with the relative ability of the three polymers to act as drag reducers [10]. Recently Ranade and Ulbrecht [6] studied the effect of CMC and Separan on the gas–liquid mass transfer in a stirred tank and found that Separan is more effective than CMC in reducing the mass transfer coefficient. This agrees with the present finding. The difference in effectiveness between the three polymers is accounted for by the difference in molecular weight and chain flexibility [11, 12]. The higher the molecular weight and chain flexibility, the greater the ability of the polymer molecule to damp turbulent eddies [10–12]. Among the three polymers, Polyox has the highest molecular weight and its molecules are the most flexible [13–15].

Table 1 shows that the percentage reduction in the mass transfer coefficient is insensitive to polymer concentration within the range 10–100 ppm. For higher polymer concentrations, e.g. 200 ppm, the percentage reduction in the mass transfer coefficient increases substantially. This may be explained by the fact that at high polymer concentration, solution viscosity increases significantly and contributes to the decrease in the rate of mass transfer. It would be of interest to compare the present results for CMC and Polyox with previous work in alkaline and acid solutions conducted under similar conditions in order to shed

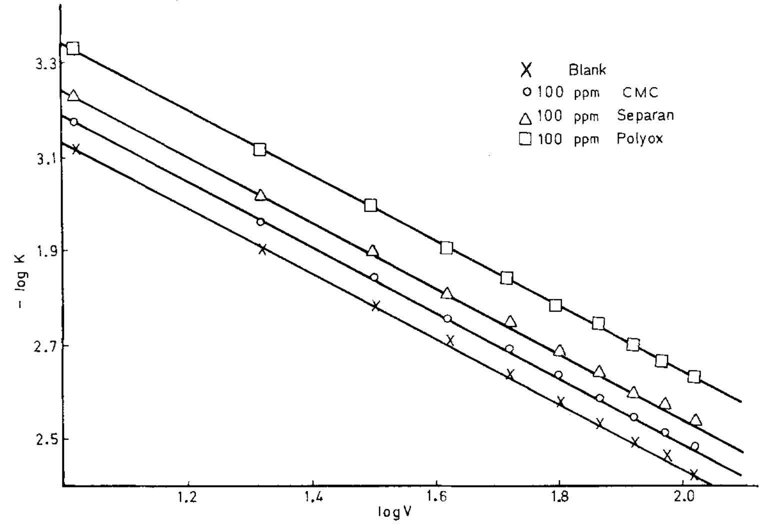

Fig. 2. Effect of cylinder rotational speed on the mass transfer coefficient for different polymer solutions.

some light on the role played by the nature of the medium on the performance of the polymer. Comparison of the effect of Polyox on the percentage reduction in the mass transfer coefficient in alkaline, acid and neutral media shows that the nature of the medium has in general little effect on the performance of the polymer. It is probable that the supporting electrolytes used differ only slightly in their effect on the degree of polymer expansion which determines the ability [16–19] of a given polymer molecule to act as a drag reducer. Electrolytes can decrease polymer expansion through interionic attraction with the polymer ions in the case of ionic polymers [20, 21] (e.g. CMC) and/or decreasing the degree of polymer solvation in the case of non-ionic polymers [22]. A comparison of the effect of CMC on the percentage reduction in the mass transfer coefficient in alkaline and neutral media shows that the performance of CMC is only slightly affected by the nature of the medium except at high CMC concentrations (e.g. 200 ppm) where the polymer becomes a more effective mass transfer reducer in neutral solutions than in alkaline solutions. This is explained by the fact that the viscosity of the CMC solution decreases with increasing pH [15], i.e. the adverse viscosity effects of CMC on the rate of mass transfer which appear at high CMC concentrations (i.e. 200 ppm) become less severe in alkaline solutions.

In view of the chemical instability of Separan in

Table 1. Effect of polymer solutions on the percentage reduction in mass transfer coefficients at different rotational speeds

Rotational speed (rev min^{-1})	*Percentage reduction in* K											
	Polyox (ppm)				*Separan* (ppm)				*CMC* (ppm)			
	10	50	100	200	10	50	100	200	10	50	100	200
200	37.94	37.81	38.21	46.11	20.03	20.95	22.00	30.04	10.01	10.94	11.99	16.47
400	37.96	38.12	38.28	46.01	20.01	20.97	22.01	29.98	9.97	11.00	11.96	16.99
600	38.10	37.94	38.00	46.00	20.00	20.97	22.00	30.00	10.00	10.97	12.00	16.79
800	37.94	38.00	38.00	46.70	19.97	20.96	21.96	30.00	9.99	10.98	11.97	16.89
1000	37.99	38.08	38.16	47.16	19.97	21.00	21.98	30.00	9.99	10.97	12.00	16.90
1200	38.16	37.98	38.01	45.90	19.98	20.99	21.96	30.00	9.99	10.96	12.01	17.02
1400	38.22	38.05	38.45	45.99	20.00	20.98	21.99	30.00	10.00	10.98	11.99	17.00
1600	37.99	37.95	38.11	46.07	19.99	21.00	22.00	30.00	9.98	10.90	12.00	16.99
1800	37.95	38.07	38.01	45.96	19.99	20.99	22.01	29.99	10.00	10.99	11.98	16.99
2000	37.97	38.00	38.05	45.98	20.00	21.00	22.00	29.99	9.99	10.99	11.99	17.00

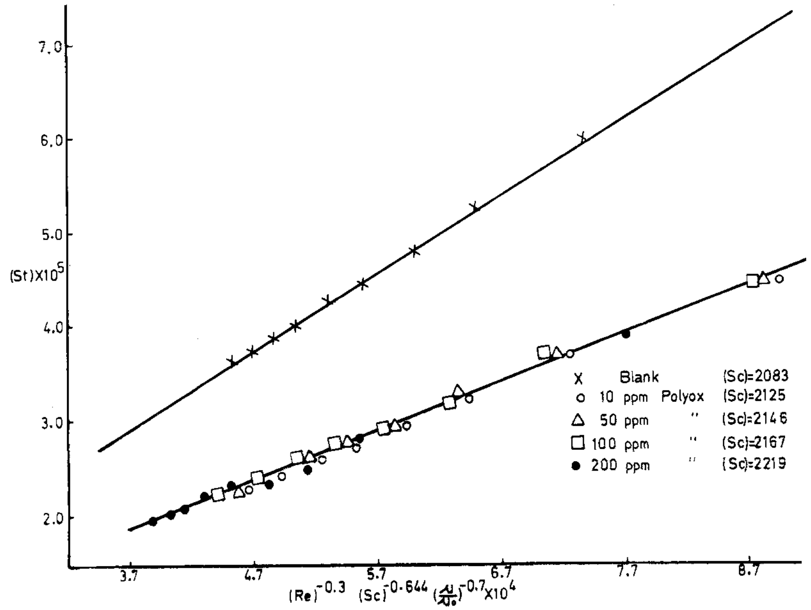

Fig. 3. Overall mass transfer correlation for solutions with and without Polyox at the rotating cylinder electrode.

alkaline and acid solutions no study could be made on its performance in these solutions.

Figs. 3–5 show that the mass transfer data in the three polymer solutions can be represented by the following correlations:

For Polyox solutions

$$(St) = 0.051(Re)^{-0.3}(Sc)^{-0.644}(u/u_0)^{-0.7} \qquad (2)$$

with an average deviation of 2.76%.

For Separan solutions

$$(St) = 0.065(Re)^{-0.3}(Sc)^{-0.644}(u/u_0)^{-0.7} \qquad (3)$$

with an average deviation of 3.27%.

For CMC solutions

$$(St) = 0.75(Re)^{-0.3}(Sc)^{-0.644}(u/u_0)^{-0.5} \qquad (4)$$

with an average deviation of 3.9%. The (Re) exponent (−0.3) was obtained by plotting log (St) versus log (Re) for different polymer concen-

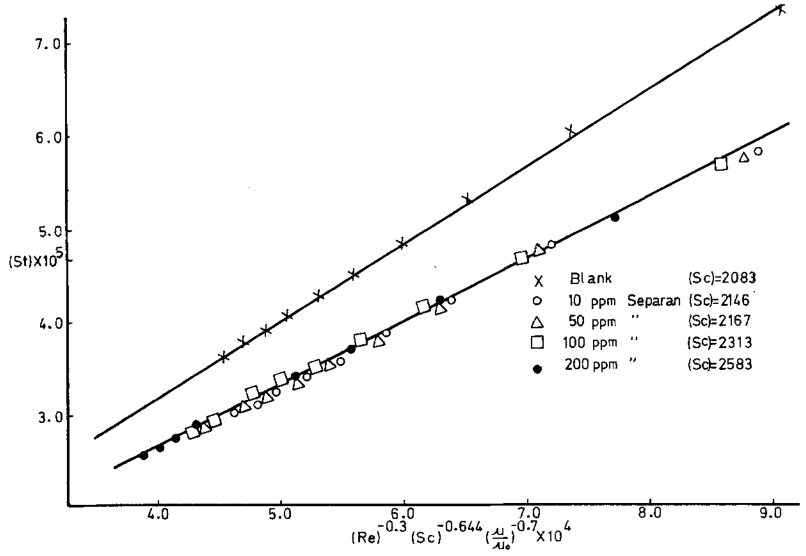

Fig. 4. Overall mass transfer correlation for solutions with and without Separan at the rotating cylinder electrode.

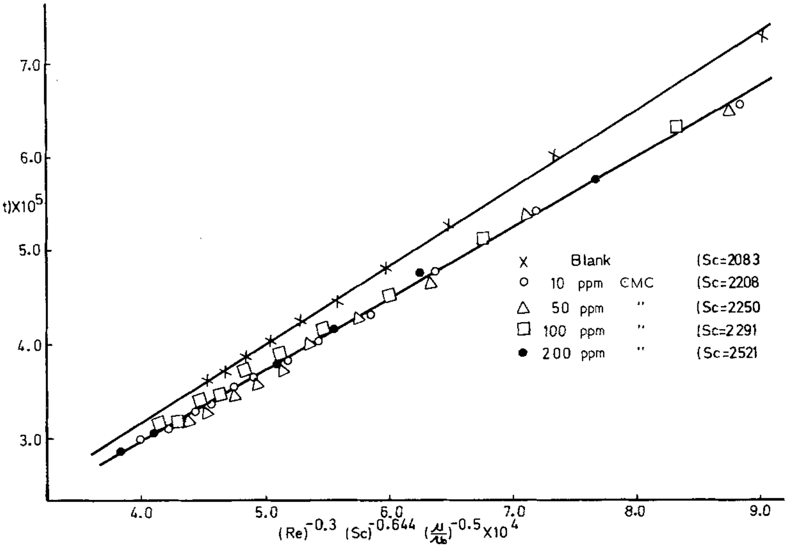

Fig. 5. Overall mass transfer correlation for solutions with and without CMC at the rotating cylinder electrode.

trations; the value of the (*Re*) exponent is consistent with the finding that the mass transfer coefficient is proportional to the linear velocity to a power of 0.7 as shown in Fig. 2. In view of the close values for (*Sc*) with 10, 50, 100 ppm solutions, it was difficult to find the exponent of (*Sc*) using the experimental data, so the value of the exponent was fixed at the value − 0.644. To include the data of 200 ppm solution in the mass transfer correlation it was found necessary to introduce a dimensionless viscosity term into the equation. The same procedure was followed in a previous work dealing with polymer solutions of concentrations higher than 100 ppm [2]. A comparison of Equation 2 with the corresponding equations obtained in previous work for acid and alkaline solutions, shows that the dimensionless viscosity term appears for high Polyox concentrations (e.g. 200 ppm); the comparison also shows that the equation obtained for acid media (6 M H_3PO_4) predicts mass transfer coefficients slightly lower than those predicted from Equation 2. This may be due to the slight difference in the effect of varying supporting electrolytes on the degree of Polyox solvation and the conformation of its molecules. A comparison of Equation 4 with the corresponding equation obtained in previous work for alkaline media shows that in alkaline medium the dimensionless viscosity term disappears because, as mentioned before, alkalinity reduces the viscosity of CMC solution.

It is worthwhile to compare the present mass transfer data with mass transfer between a tube wall and a turbulently flowing drag-reducing solution [5, 7, 23, 24]. The striking difference between the two situations is that the percentage reduction in the mass transfer coefficient in the case of rotating cylinders is insensitive to (*Re*) within the range studied, while in case of flow-through tubes it increases with (*Re*). To explain this discrepancy a basic study on the turbulence structure at both surfaces is needed along with a clearer understanding of the mechanism of the phenomenon of drag reduction by polymer addition.

References

[1] G. H. Sedahmed, B. A. Abdel-El-Naby and A. Abdel-Khalik, *J. Appl. Electrochem.* 8 (1978) 473.
[2] *Idem*, *Corros. Sci.* 17 (1977) 865.
[3] *Idem*, *J. Appl. Electrochem.* 7 (1977) 355.
[4] G. Fortuna and T. J. Hanratty, *CEP Symposium Series* 67 (1971) 90.
[5] G. A. McConaghy and T. J. Hanratty, *Amer. Inst. Chem. Eng. J.* 23(1977) 493.
[6] V. R. Ranade and J. J. Ulberecht, *ibid* 24 (1978) 796.
[7] P. S. Virk and T. Suraiya, *Proceedings 2nd International Conference on Drag Reduction (BHRA)* G3-41 (1977).
[8] A. J. Arvia, J. C. Bazan and J. S. W. Carrozza, *Electrochim. Acta* 13 (1968) 81.

[9] V. G. Levich, 'Physiochemical Hydrodynamics' Prentice Hall Inc, Englewood Cliffs, N.J. (1962).

[10] J. W. Hoyt, *ASME J. Basic Eng.* **94** (1972) 258.

[11] G. Liaw, J. L. Zakin and G. K. Patterson *Amer. Inst. Chem. Eng. J.* 17 (1971). 391.

[12] C. Balakrishnan and R. J. Gordon, *J. Appl. Polym. Sci.* 19 (1975) 909.

[13] G. K. Patterson, J. L. Zakin and J. M. Rodriquez, *I and EC (Fundamentals)* **61** (1969) 22.

[14] Union Carbide Bulletin, Polyox, F-44029A (1973).

[15] Hercules Bulletin, Sodium carboxymethylcellulose (1971).

[16] D. White and R. J. Gordon, *Amer. Inst. Chem. Eng. J.* **21** (1975) 1027.

[17] G. T. Pruitt, B. Rosen and H. R. Crawford, Western Co, Dallas, Texas, Report No. DTMB-2 (1966).

[18] C. A. Parker and A. H. Hedley, *Nature Phys. Sci.* (1972) 236.

[19] O. K. Kim, R. C. Little and R. T. Ting, *CEP Symposium Series* **69** (1973) 39.

[20] M. A. Frommer, A. Feder-Lavy and M. A. Kraus, *J. Coll. Inter. Sci.* 48 (1974) 165.

[21] D. Shah and B. Ecanow, *J. Pharmaceut. Sci.* **63** (1974) 1164.

[22] R. C. Little, Naval Research Laboratory Report 6542 (1967).

[23] G. H. Sedahmed and R. G. Griskey, *Amer. Inst. Chem. Eng. J.* **18** (1972) 134.

[24] G. H. Sedahmed, M. S. Abdo, H. A. Farag and S. Tantawy, to be published.