

# Electrochemical mass transfer in solutions containing drag-reducing polymers

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Electrochemical mass transfer was studied in the presence of polyethylene oxide as a drag-reducing agent using the cathodic reduction of  $K_3Fe(CN)_6$  at a rotating cylinder electrode over a range of Reynolds numbers from 4100-41 000. Solutions containing polymer showed a lowered mass transfer coefficient than that without polymer. Mass transfer data in solutions containing polymers was found to fit the correlation:

$$(St) = 0.0475 (Re)^{-0.3} (Sc)^{-0.644}.$$

A comparison was made between the reduction in friction and the rate of mass transfer; it was found that at relatively low ( $Re$ ) values, the reduction in the rate of mass transfer is higher than the reduction in friction, whilst at relatively high ( $Re$ ) values, the reverse is true.

## List of symbols

- $I_L$  = limiting current density,  $A\ cm^{-2}$   
 $Z$  = number of electrons involved in the reaction  
 $F$  = Faraday (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,  $cm$   
 $\mu', \mu_0$  = viscosity of solutions with and without polymers respectively,  $P$   
 $\rho$  = density,  $g\ cm^{-3}$   
 $C$  = concentration of  $Fe(CN)_6^{3-}$  ions,  $mol\ cc^{-1}$   
 $(St)$  = Stanton number =  $K/V$   
 $(Sc)$  = Schmidt number =  $\nu/D$   
 $(Re)$  = Reynold number =  $\rho Vd/\mu$

## 1. Introduction

The decrease in frictional resistance which occurs when a minute quantity of certain soluble high molecular weight polymers is added to a fluid in turbulent flow is known as drag reduction. This phenomenon was first studied systematically by Toms [1] and has been the subject of extensive

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investigation in the past decade [2-5]. The practical application of drag reduction in chemical processing, pipelines, ship technology and other areas has motivated much of this work. More fundamental studies of drag reducing solutions have focused on gaining a better understanding of their rheological behaviour and influence on the physics of turbulent flow. Although the exact mechanism of drag reduction by polymer addition is not clearly understood, there is considerable evidence to suggest that turbulent drag reduction can be interpreted as a thickening of the viscous laminar sublayer caused by a damping of the eddies near the conduit wall by the polymer molecules.

The object of this investigation is to introduce the phenomenon of drag reduction to the electrochemical field with special reference to the effects of polymer additions on the rates of mass transfer in electrochemical processes. In the electrochemical industry turbulent flow is used to enhance the rates of mass transfer in electrochemical reactors used to conduct diffusion-controlled reactions e.g. electrowinning of metals, electro-organic and inorganic syntheses and electrochemical machining. Corrosion which is electrochemical in nature is enhanced by turbulent flow. The use of drag-reducing polymers in electrochemical processes

would lead to a decrease in the rate of mass transfer through a thickening of the diffusion layer. In this work the extent to which the rate of mass transfer is decreased under different conditions is studied.

The cathodic reduction of  $K_3Fe(CN)_6$  at a rotating nickel cylinder electrode was chosen for the present study because it is well-known to be a diffusion-controlled reaction [6]. Polyethylene oxide (Polyox), a very effective drag-reducing agent, was chosen because it is chemically compatible with the electrolyte used [7]. The mass transfer coefficient was obtained from the limiting current using the equation:

$$K = I_L/ZFC. \quad (1)$$

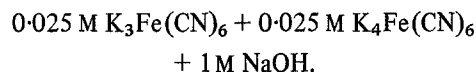
## 2. Experimental technique

Polyethylene oxide (Polyox WSR 301), a product of the Union Carbide Chemical Co., was chosen as the drag reducing agent.

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 cell. The cell consisted of a nickel-plated copper cylinder cathode of diameter 2 cm rotating in the centre of a 10 cm i.d. 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 an anode. The cathode was driven by a variable speed motor over the range 200–2000 rev min<sup>-1</sup>. Special precautions were taken to eliminate 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 as that used in the cell; the tip of the capillary end of the luggin tube was placed at 0.5–1 mm from the rotating cylinder.

Three polymer concentrations were used: 10, 50, 100 ppm. In all cases, the electrolyte used was composed of:



NaOH acts as a supporting electrolyte to prevent ionic transfer by electrical migration.

The viscosities and densities of the solutions were determined using Ostwald's viscometer and a density bottle respectively; the diffusivity of  $K_3Fe(CN)_6$  in different solutions was determined using a 1.52 cm diameter rotating disc nickel-plated copper cathode in the laminar flow regime; the diffusion coefficient was calculated using the Levich equation [8]:

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

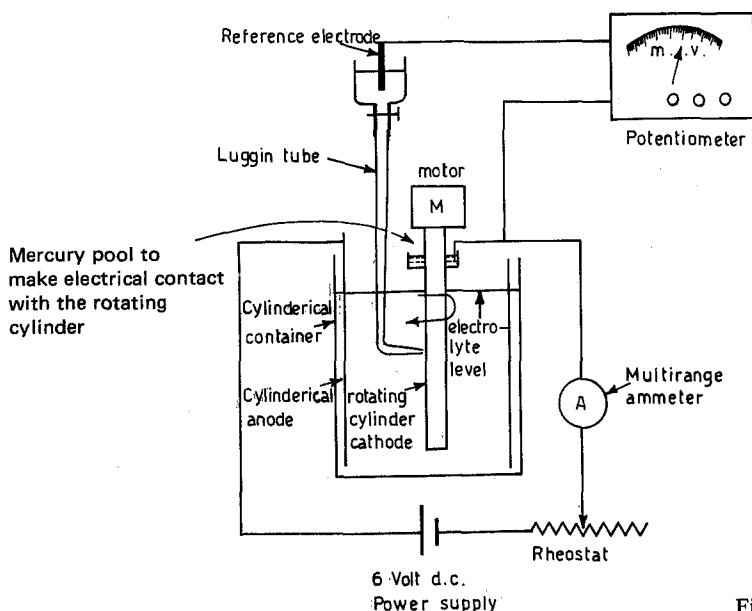


Fig. 1. Cell and electrical circuit.

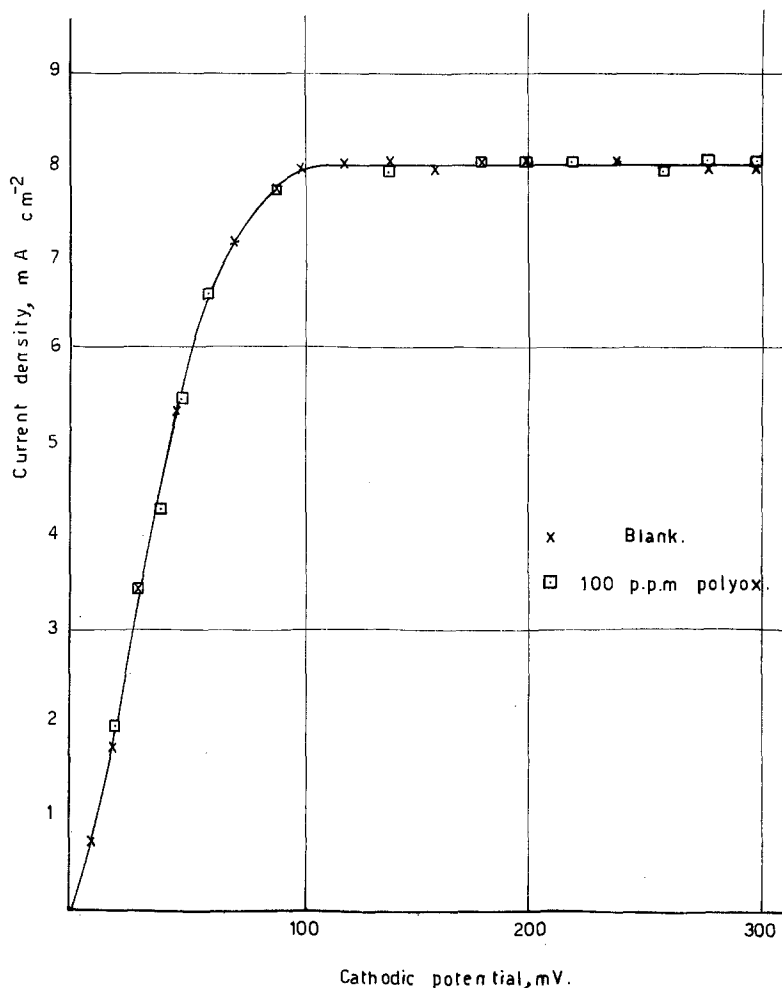


Fig. 2. Effect of polymer addition on polarization at the rotating disc electrode in the laminar flow region. Disc diameter = 1.52 cm; temperature = 25°C;  $\text{rev min}^{-1}$  = 600.

### 3. Results and discussions

Figs. 2 and 3 show the effects of polyox additions on the current-potential relation and the limiting current in the case of a rotating disc electrode (laminar flow) and a rotating cylinder (turbulent flow) respectively; Polyox decreases the limiting current in the turbulent flowcase whilst in the laminar flowcase it has no effect. This is consistent with the proposed mechanism of action of drag-reducing polymers.

Fig. 4 represents the relation between the limiting current and the square root of the angular velocity of the rotating disc under laminar flow conditions in different polymer solutions; the relation is linear and agrees with the Levich equation.

Fig. 5 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 polyox concentration: the data fit the relation

$$K = aV^{0.7}. \quad (3)$$

The velocity exponent is in agreement with the value reported by Eisenberg *et al.* [6] who studied mass transfer at rotating cylinders in polymer-free solutions.

An overall mass transfer correlation of the data was sought in terms of the dimensionless groups ( $St$ ), ( $Sc$ ) and ( $Re$ ) as shown in Fig. 6; for polymer-free solutions, the data were found to fit the equation:

$$(St) = 0.0791 (Re)^{-0.3} (Sc)^{-0.644} \quad (4)$$

with an average deviation of 0.9%. The data are in agreement with that of Eisenberg *et al.* [6]. In solutions containing polyox, the mass transfer data were found to fit the equation:

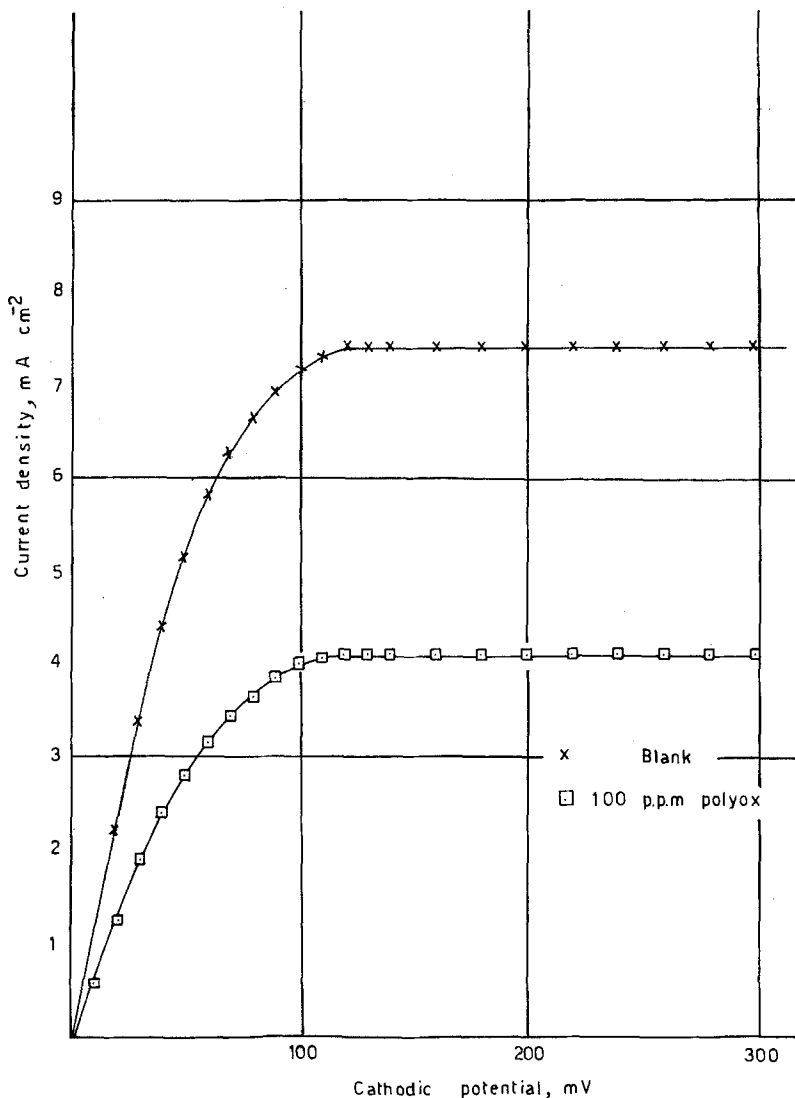


Fig. 3. Effect of polymer addition on polarization of the rotating cylinder electrode in the turbulent flow regime. Cylinder diameter = 2 cm; temperature = 25°C; rev min<sup>-1</sup> = 1000.

$$(St) = 0.0475 (Re)^{-0.3} (Sc)^{-0.644} \quad (5)$$

with an average deviation of 6.3%.

Table 1 and Fig. 5 show that within the range of polyox concentration studied here (10–100 ppm) the percentage reduction in the rate of mass transfer is insensitive to polymer concentration; this is in agreement with the findings of Sedahmed and Griskey [7].

In order to compare the effect of drag-reducing agents on the process of mass and momentum transfer, Equation 5 was extrapolated to the higher Reynolds numbers investigated by Killen and Almo [9] who studied the effect of polyox on the friction coefficient at rotating cylinders;

Table 1. Effect of polyox on the % reduction in mass transfer coefficient

(Re)	% Reduction in K		
	10 ppm	50 ppm	100 ppm
4 183	45.3	40.0	42.1
8 365	46.5	48.4	45.2
12 560	45.4	41.5	43.9
16 743	45.2	46.0	44.0
20 925	45.1	44.1	45.8
25 120	44.8	46.3	46.3
29 303	44.5	45.3	46.7
33 485	45.8	48.2	47.0
38 058	45.0	46.1	46.1
41 863	44.2	46.3	45.3

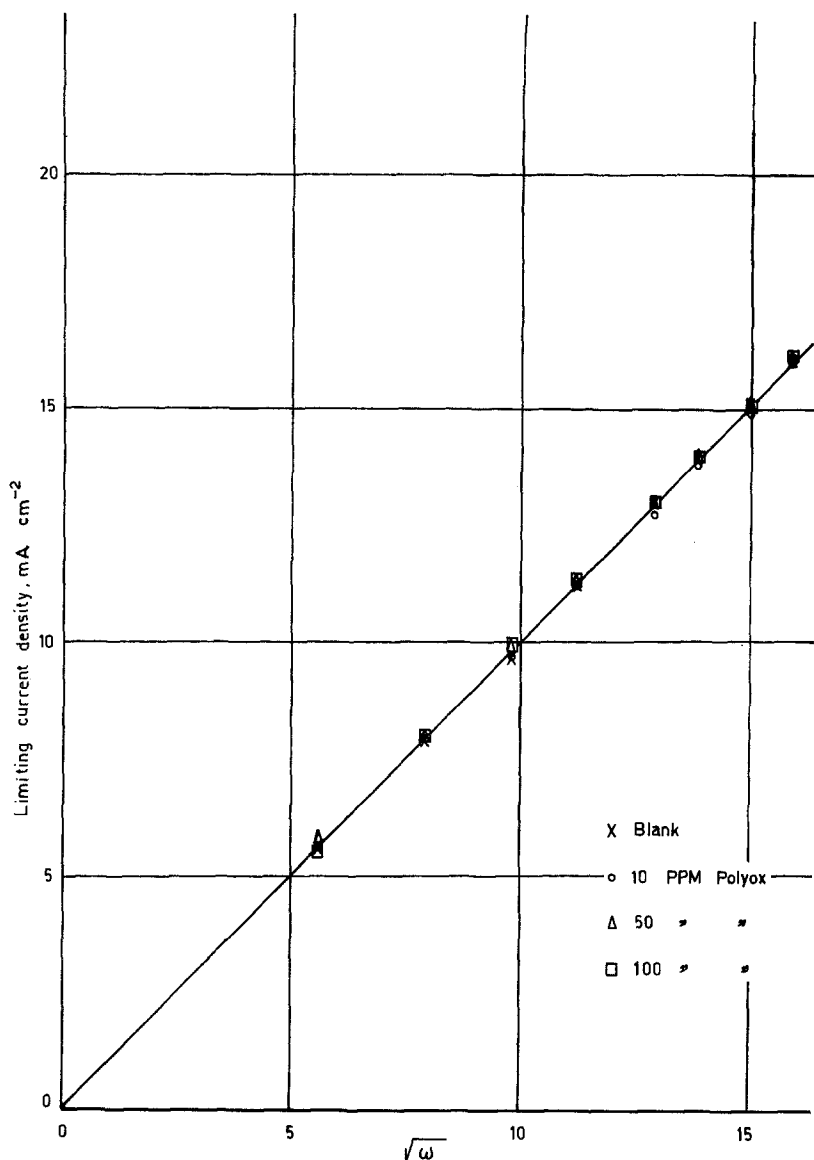


Fig. 4. Cathodic limiting current versus angular disc velocity for different concentrations of polyox.

Table 2. Comparison between the % reduction in the mass transfer coefficient and friction coefficient for 50 ppm polyox

(Re)	% Reduction in the mass transfer coefficient	% Reduction in the friction factor [9]
2 700 000	42.1	62.2
1 700 000	42.1	60.0
1 000 000	42.1	57.8
4 500 000	42.1	52.6
3 000 000	42.1	40.5
1 700 000	42.1	37.5

Table 2 shows that the % reduction in the friction factor is higher than that in the mass transfer coefficient at relatively high ( $Re$ ) numbers. The reverse is true at relatively low ( $Re$ ) numbers.

Buston and Glass [10] studied the effects of drag-reducing agents on the rate of mass and momentum transfer in pipes and found that the percentage reduction in the friction coefficient is higher than that in the rate of mass transfer while McConaghy [11], who made a simultaneous study of mass and momentum in a tube, found that the percentage reduction in the friction coefficient is less than that in the rate of mass transfer.

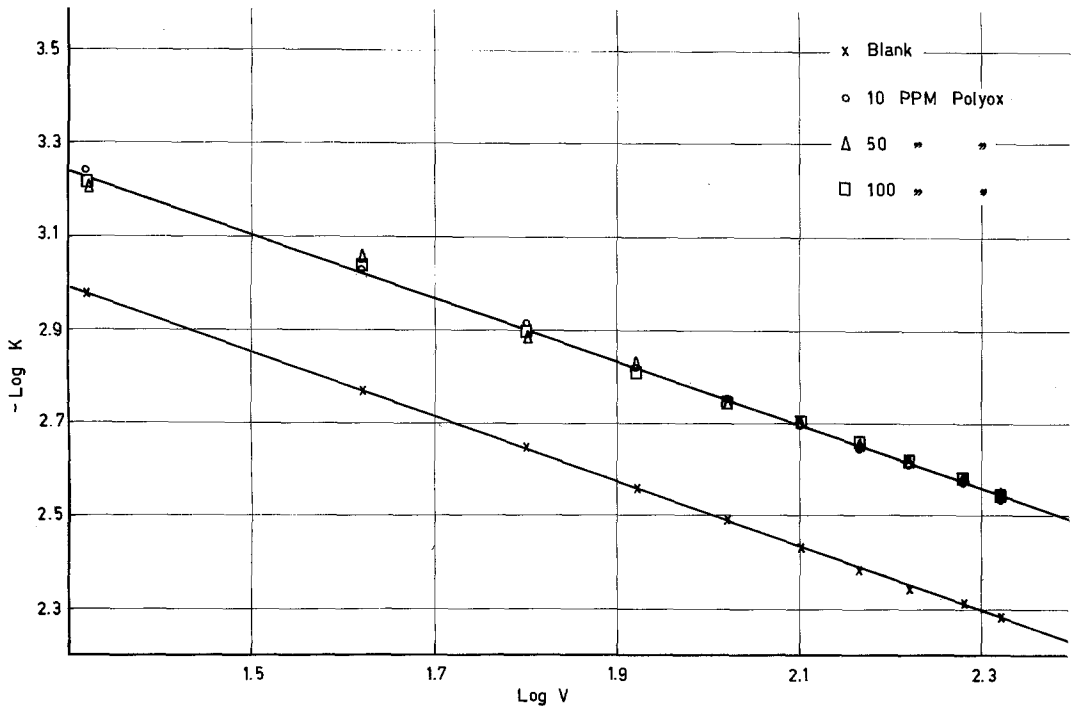


Fig. 5. Effect of cylinder rotational speed on the mass transfer coefficient.

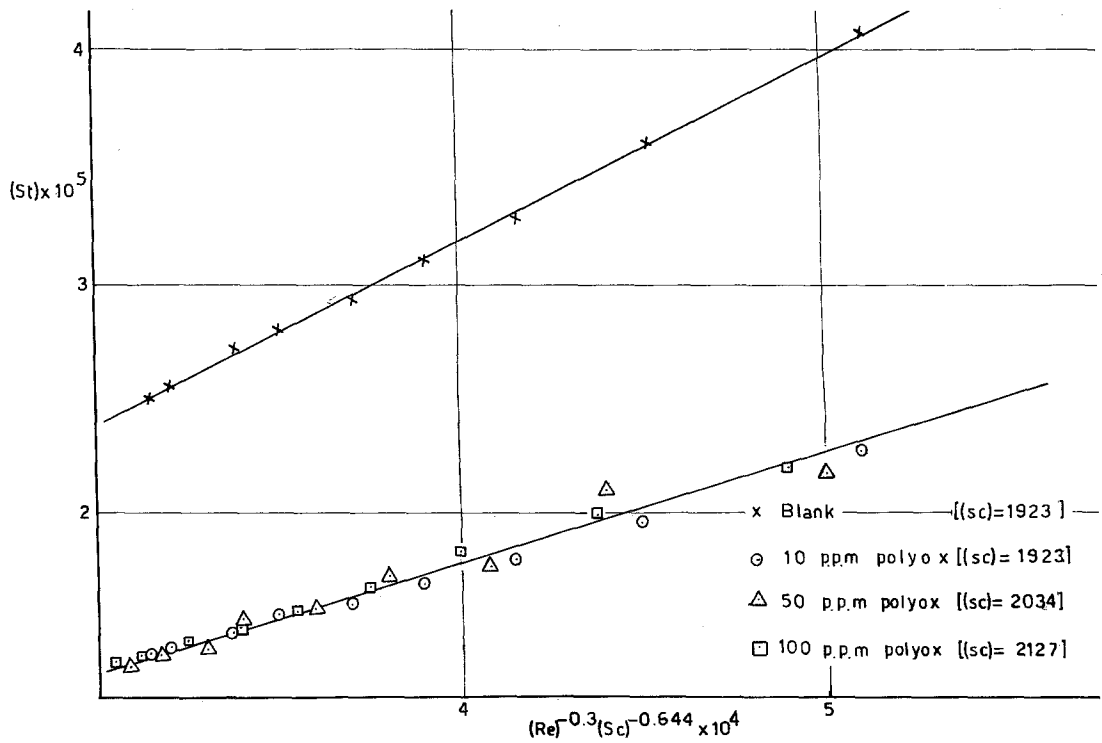


Fig. 6. Overall mass transfer correlations for solutions with and without polymers at the rotating cylinder electrode.

In view of the aforementioned results, drag-reducing agents should be applied to electrochemical processes under conditions where the % reduction in mass transfer is far less than the % reduction in friction otherwise the lowering in the rate of production due to the decrease in the rate of mass transfer will outweigh the benefits gained by the reduction in the drag and the pumping costs. As for corrosion, drag-reducing polymers can be applied without reservation because any decrease in the rate of mass transfer will result in a corresponding decrease in the rate of corrosion i.e. in this case drag-reducing polymers will act as corrosion inhibitors as well as drag-reducers e.g. in pipelines.

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#### References

- [1] B. A. Toms, *Proc. Int. Cong. Rheol.* Vol II, North Holland Pub. Co., Amsterdam, (1949) p. 135.
- [2] G. E. Gadd, *Nature* **212** (1966) 874.
- [3] *Idem*, *Nature Phys. Sci.* **230** (1971) 29.
- [4] A. G. Fabula, *Proc. 4th. Int. Cong. Rheol.* Wiley, New York 3 (1965) 455.
- [5] P. S. Virk, E. W. Merrill, H. S. Mickley and K. A. Smith, *J. Fluid Mech.* **30** (1967) 305.
- [6] M. Eisenberg, C. W. Tobias and C. R. Wilke, *J. Electrochem. Soc.* **101** (1954) 307.
- [7] G. H. Sedahmed and R. G. Griskey, *A.I.Ch.E.J.* **18** (1972) 138.
- [8] V. G. Levich, 'Physiochemical Hydrodynamics', Prentice Hall Inc, Englewood Cliffs, N.J. (1962).
- [9] J. M. Killen and J. Almo, *Proc. Symp. viscous drag-reduction* Plenum Press, New York (1969) p. 447.
- [10] J. Buston and D. H. Glass, *Proc. Int. Conf. drag-reduction* (1974) Cranfield Bedford, BHRA, P.A 3-41.
- [11] G. A. McConaghy, Ph.D thesis, University of Illinois (1974).