Mass Transfer in Drag Reducing Fluid Systems

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The effect of drag reducing agents on mass transfer in fluid systems was studied. The mass transfer was determined by an electrochemical technique which involved transport of mass from the fluid to the tube wall. It was found that the drag reducing agents retarded mass transfer in turbulent but not in laminar systems. The effect on mass transfer was shown to be comparable to that on heat transfer. The Wells correlation for heat transfer reducing systems was employed for mass transfer. In addition, correlations for Stanton number were determined for mass transfer in drag reducing systems.

Role Indicator	Terms
D	Drag reducing agents
E	Drag reduction
H	Mass transfer
J	Electrochemical technique
D	Polyox solutions
H	Turbulent systems
H	Laminar systems
H	Schmidt number
H	Prandtl number
H	Momentum transfer
H	Heat transfer
H	Stanton number
H	Mass transfer entry region

The addition of small amounts of high molecular weight polymers to fluids can produce significant reductions in turbulent pipe flow friction. Such fluid systems are termed drag reducing fluids. The application of this effect is attractive in many industrial situations involving momentum transfer because of a lessening of energy dissipation. The gains realized, however, may become questionable if other transport processes (heat or mass transfer) are involved, since there may be serious decreases in heat or mass transfer rates in drag reducing fluids.

Studies of other transport processes in drag reducing fluids have been limited in contrast to an extensive literature (*1* to *36*) on the momentum transfer aspect. There have been no published studies on mass transfer in drag reducing systems and only a few investigations on heat transfer (*37* to *43*). The present work was undertaken to determine the effect on mass transfer in drag reducing fluid systems.

APPARATUS AND EXPERIMENTAL PROCEDURE

Polyox solutions were used as the drag reducing fluids in the present study, since prior investigations had considered both momentum transfer (*11*) and heat transfer (*41*) in these systems. Mass transfer was studied by an electrochemical technique which involved transport of mass from the fluid to the tube wall. This method was preferable to the soluble tube wall technique, since the latter led to roughness which interfered with mass transfer. The background of the electrochemical technique has been described by Hanratty and co-workers (*45* to *47*).

The actual rate of mass transfer in this work was determined by measuring the limiting current of the cathodic reduction of $K_3Fe(CN)_6$. The solutions used in the research were a blank solution (0.025M $K_3Fe(CN)_6$ and 0.025M $K_4Fe(CN)_6$ in 1M NaOH) and a polymer solution (blank solution plus a given ppm of polymer). The polymer used in this work was Polyox WSR301, a Union Carbide product. This material is an effective drag reducing agent and was chemically stable under the conditions used in the present study. This stability was demonstrated not only in earlier studies (*11*, *41*) but also in this work. Polymer molecular weight was 6×10^6.

Three concentrations of polymer solutions (10, 50, 100 ppm.) were studied. All solutions were Newtonian in flow behavior. In

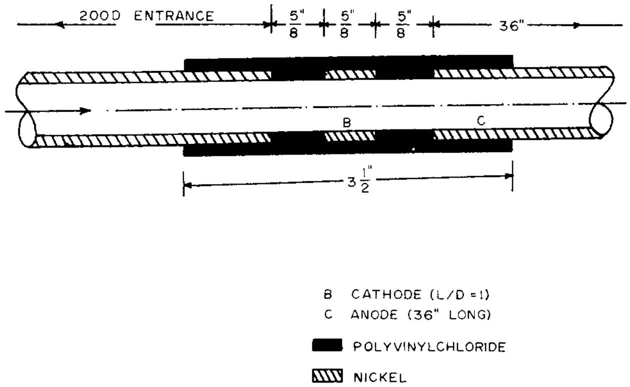

Fig. 1. Test section.

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addition, their densities and viscosities were essentially the same. The diffusion coefficient of ferricyanide ion was taken from the literature (*44, 45*).

The investigation was carried out in the device shown in Figure 1. The mass transfer section was preceded by a nickel tube 200 diameters long. This tube segment served as an entrance section so that there would be hydrodynamically fully developed flow at the cathode. The electrochemical reaction took place (Figure 1) between the cathode (a ⅝ in. long nickel ring) and the anode (a 3-ft. long nickel ring). The cathode was separated electrically both from the entrance section and the anode by polyvinylchloride rings.

It should be noted that the mass transfer entry length was $L/D = 1.0$. The study was limited to this situation because inordinately high rates of liquid flow (that is, $N_{Re} >>> 100{,}000$) would be needed for fully developed mass transfer (*46, 45*).

Before each run the cathode was cleaned with carbon tetrachloride and buffed with rough paper. Next, the cathode was activated by treating it cathodically in a 5% sodium hydroxide solution at a current density of 20 ma. for about 10 min.

Limiting current for the cathode was determined by increasing applied potential stepwise and recording the corresponding current until a plateau was obtained on the current potential curve. These curves were similar in shape to those observed by Hanratty (*47*). For such conditions the current is controlled by the rate of mass transfer of ferricyanide ion to the surface of the working cathode (where the ferricyanide concentration is zero). Mass transfer coefficients and rates were then obtained from the limiting current data using the relation

$$N = \frac{i}{ZFA} = KC \qquad (1)$$

The value of current used in Equation (1) was that at the midpoint of the plateau portion of the curves in Figure 3.

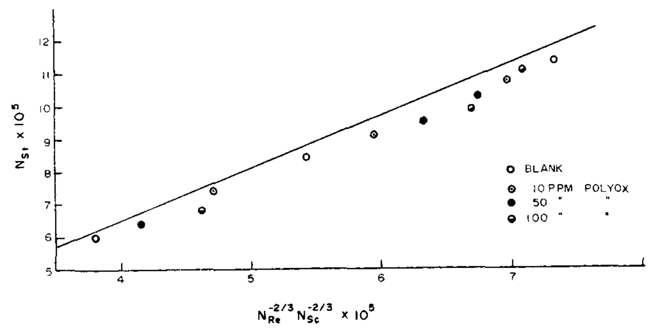

Fig. 2. N_{St} versus $N_{Re}^{-2/3}\, N_{Sc}^{-2/3}$ in laminar region.

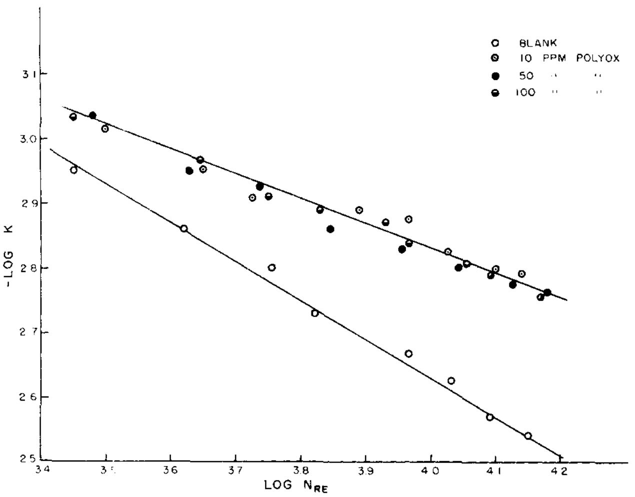

Fig. 3. Effect of drag reducing agent on mass transfer coefficient in the turbulent region.

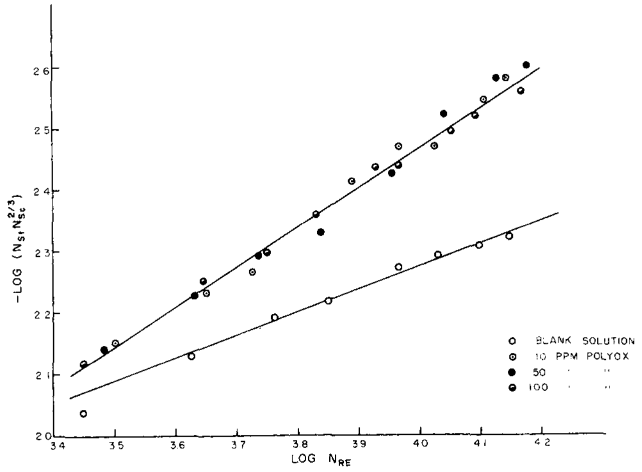

Fig. 4. $N_{St}\, N_{Sc}^{2/3}$ versus N_{Re} in turbulent region.

RESULTS

Data was determined in both the laminar and turbulent flow regions. All data were determined in the mass transfer entry region (that is, L/D for mass transfer $= 1$).

In the laminar region it was found that the data (Figure 2) both for the blank and the polymer solution fit the Leveque equation.

$$N_{St_{AB}} = 1.61\, N_{Re}^{-2/3}\, N_{Sc}^{-2/3} \qquad (2)$$

These results not only checked the validity of the experimental procedure but also showed that the ferricyanide ion diffusion coefficient was unaffected by the trace addition of the polymer to the solution.

As a further check Hanratty's data (*45*) for mass transfer L/D of 1.0 were compared to those for the blank solution in the present work. It was found that both Hanratty's and the blank solution data could be fit by the correlation

$$N_{St} = 0.1116\, N_{Sc}^{-2/3}\, N_{Re}^{-0.33} \qquad (3)$$

with a deviation of only 3.5%.

Figures 3 and 4 summarize the turbulent data. In Figure 3 the effect of the drag reducing agent is clearly seen in the decreased values of the mass transfer coefficient. Likewise in Figure 4 the correlation of the Stanton number also shows the deleterious effect of the drag reducing agent. The correlation for the fluids with polymer is

$$N_{St_{AB}} = 0.06\, N_{Sc}^{-2/3}\, N_{Re}^{-0.30} \qquad (4)$$

The works of two sets of authors in particular were relevant. The first of these was that of Virk and Merrill, who studied both momentum and heat transport in polyox solutions (*11, 41*). The other was the study of Wells (*43*), who developed a general correlation between heat and momentum transfer in drag reducing systems.

Wells correlation written for mass transfer is

$$N_{St_{AB}} = \frac{f/2}{1.02\,\dfrac{uL}{u^*}\left(\dfrac{f}{2}\right)^{1/2}(N_{Sc}-1)\,(N_{Sc})^{-1/3} + 1.2} \qquad (5)$$

In addition, Virk and Merrill (*11*) have shown for polyox drag reducing systems (at maximum drag reduction).

$$f/2 = 0.21\, N_{Re}^{-0.55} \qquad (6)$$

Stanton numbers were calculated using Equations (5) and (6) together with additional momentum transfer data (*11*). A comparison of the Stanton numbers calculated with Wells equation and experimental data is shown in

Table 1. As can be seen, the % errors are large (average % error of 20.5%).

One factor which could account for the divergence of calculated and experimental data was that the former were for fully developed mass transfer, while the latter were for a mass transfer length of 1.0. A possible method of compensating for this was to use the work of Hanratty (*45*). This author presented for Newtonian fluids a correlation of Stanton number versus Reynolds number with mass transfer L/D as a parameter. It was felt that if the data calculated from Wells correlation were converted to an L/D of 1.0 they might check the experimental data more closely. This was done and the results are shown in Table 2. As can be seen, the % errors are reduced (average error 13.6%).

The % errors obtained with the length correction are, however, reasonable when compared to the errors obtained by Wells (*43*) in his work on heat transfer. The average % error for the heat transfer study was 19.7%. On this basis, it would appear that mass transfer in drag reducing systems correlates with heat transfer in such systems.

Table 1. Comparison Experimental Mass Transfer Stanton Numbers with Values Calculated from Wells (*43*) Correlation

N_{Re}	Experimental $N_{St_{AB}} \times 10^5$	Calculated $N_{St_{AB}} \times 10^5$	% Error of calculated values
14,960	1.762	1.278	20.4
14,908	1.775	1.288	20.6
13,904	1.891	1.333	13.6
13,340	1.920	1.348	21.8
12,778	1.988	1.375	19.3
12,421	2.037	1.403	19.0
11,363	2.120	1.445	22.8
11,090	2.170	1.470	23.8
10,648	2.221	1.480	23.1

Table 2. Comparison Experimental Mass Transfer Stanton Numbers with Wells (*43*) Correlation Values Corrected for Length

N_{Re}	Experimental $N_{St_{AB}} \times 10^5$	Calculated $N_{St_{AB}} \times 10^5$	% Error of calculated values
14,960	1.762	1.592	10.7
14,908	1.775	1.622	9.4
13,904	1.891	1.542	22.6
13,340	1.920	1.723	11.4
12,778	1.988	1.666	11.9
12,421	2.037	1.769	15.2
11,363	2.120	1.874	14.3
11,040	2.170	1.929	12.5
10,648	2.221	1.923	14.7

Table 3. Comparison Experimental Mass Transfer Stanton Numbers with Merrill (*41*) Correlation Values Corrected for Length

N_{Re}	Experimental $N_{St_{AB}} \times 10^5$	Calculated $N_{St_{AB}} \times 10^5$	% Error of calculated values
14,960	1.762	1.422	19.3
14,908	1.775	1.437	19.0
13,904	1.891	1.550	18.0
13,340	1.920	1.580	17.7
12,778	1.988	1.617	18.7
12,421	2.037	1.693	16.9
11,363	2.120	1.762	21.6
11,090	2.170	1.824	15.9
10,648	2.221	1.865	16.0

The experimental data were also checked with Virk and Merrill's (*41*) heat transfer correlation written for mass transfer.

$$(N_{St_{AB}})\,(N_{Sc})^{0.6} = \frac{f}{2} \tag{7}$$

Calculated Stanton numbers corrected for length (as per Table 2) are shown in Table 3. As can be seen, the % errors are somewhat larger than those for Table 2 (average error 18.1%). However, it would appear that the comparison of Table 3 also indicates that mass transport and heat transport correlate in drag reducing systems.

CONCLUSIONS

On the basis of the present work, it can be concluded that the addition of a drag reducing agent decreases mass transfer rates in turbulent flow. Furthermore, the reduction in mass transfer appears to correlate with that for heat transfer. In this instance the Wells correlation (*43*) adapted for mass transfer

$$N_{St_{AB}} = \frac{f/2}{1.02\,\frac{uL}{u^*}\,(f/2)^{1/2}\,(N_{Sc}-1)\,(N_{Sc})^{-1/3} + 1.2} \tag{8}$$

can be used to estimate Stanton numbers. For short mass transfer lengths the correlation

$$N_{St_{AB}} = 0.06\,N_{Sc}^{-2/3}\,N_{Re}^{-0.30}\left(\frac{L}{D}\right)^{1/3} \tag{9}$$

should be used. An ancillary point of the present work was that Stanton numbers in Newtonian systems with a mass transfer L/D of 1.0 are best described by the relation

$$N_{St_{AB}} = 0.1116\,N_{Sc}^{-2/3}\,N_{Re}^{-0.33} \tag{10}$$

NOTATION

f = fanning friction factor
i = limiting current, amperes
u_L = axial local velocity at edge of viscous sublayer, cm./sec.
u^* = shear velocity $(\tau_w/\rho)^{1/2}$
A = area of cathode, sq.cm.
C = concentration, mole/cu.cm.
D = tube diameter, cm.
F = Faraday's constant
K = mass transfer coefficient, cm./sec.
L = electrode length, cm.
N = mass transfer flux, mole/(sq.cm.)(sec.)
N_{Pr} = Prandtl number
N_{Re} = Reynolds number
N_{Sc} = Schmidt number
N_{St} = Stanton number for heat transfer
$N_{St_{AB}}$ = Stanton number for mass transfer
Z = number of electrons involved in electrode reaction
τ_w = wall shear stress
ρ = density

LITERATURE CITED

1. Agoston, G. A., W. H. Harte, H. C. Hottel, W. A. Klemm, K. J. Mysels, H. H. Pomeroy, J. M. Thompson, *Ind. Eng. Chem.*, 46, 1017 (1954).
2. Mysels, K. J., U.S. Patent 2,492,173 (1949).
3. Toms, B. A., *Proc. Int. Cong. Rheology*, p. 135 North Holland, Amsterdam (1949).
4. Crawford, H. R., and Pruitt, G. T., Report No. DTMB-1,

prepared for David Taylor Model Basin Hydromechanical Laboratory, Washington, D. C. (1965).

5. Fabula, A. G., *Proc. 4th Intern. Congress Rheol.*, **3**, 455, Wiley, New York (1965).
6. Lummus, J. L., J. E. Fox, and D. B. Anderson, *Oil Gas J.*, **59**, 87 (1961).
7. Metzner, A. B., and M. G. Park, *J. Fluid Mech.*, **20**, 291 (1964).
8. Patterson, G. K., J. L. Zakin, and J. M. Rodriguiz, *Ind. Eng. Chem.*, **61**, 22 (1969).
9. Savins, J. G., *Soc. Pet. Eng. J.*, **4**, 203 (1964).
10. Sever, F. A., and A. B. Metzner, *Can. J. Chem. Eng.*, **45**, 121 (1967).
11. Virk, P. S., E. W. Merrill, H. S. Mickley, and K. A. Smith, *J. Fluid Mech.*, **30**, 305 (1967).
12. Wells, C. S., *Am. Inst. Aerospace Astron. J.*, **3**, 1801 (1965).
13. Elata, C., and J. Poreh, *Israel J. Technol.*, **3**, 1 (1965).
14. Meter, D. M., and R. B. Bird, *AIChE J.*, **10**, 881 (1964).
15. Meyer, W. A., *AIChE J.*, **12**, 417 (1966).
16. Elata, C., and M. Poreh, *Rheol. Acta*, **5**, 148 (1966).
17. Gadd, G. E., *Nature*, **206**, 463 (1965).
18. Singh, K., Ph.D. thesis, Pennsylvania State Univ., University Park (1966).
19. Tomita, Y., *Bulletin Jap. Soc. Mech. Eng.*, **9**, 730 (1966).
20. Astarita, G., and L. Nicodemo, *AIChE J.*, **12**, 478 (1966).
21. Fabula, A. B., Ph.D., thesis, Pennsylvania State Univ., University Park (1966).
22. Metzner, A. B., and G. Astarita, *AIChE J.*, **13**, 550 (1967).
23. Metzner, A. B., and F. A. Seyer, "Proc. 6th Naval Hydrodynamics Symp.," Office Naval Res., Washington, D. C. (1966).
24. Savins, J. G., *AIChE J.*, **11**, 673 (1965).
25. Seyer, F. A., Ph.D. thesis, Univ. Delaware, Newark (1968).
26. ———., and A. B. Metzner, *AIChE J.*, **15**, 426 (1969).
27. Metzner, A. B., and A. P. Metzner, *Rheol. Acta.*, in press.
28. Denn, M. M., and J. J. Roisman, *AIChE J.*, **15**, 454 (1969).
29. Marsh, B. D., and J. R. A. Pearson, *Rheol. Acta.*, **4**, 326 (1968).
30. Oliver, D. R., *Can. J. Chem. Eng.*, **44**, 100 (1966).
31. Seyer, F. A., M.ChE. thesis, Univ. Delaware, Newark (1965).
32. Wells, C. S., and J. G. Spangler, *Phys. Fluids*, **10**, 1890 (1967).
33. Savins, J. G., *Rheol. Acta.*, **7**, 87 (1968).
34. *Ibid.*, **6**, 323 (1967).
35. ———., paper presented at Symposium on Viscous Drag Reduction, LTV Research Center, Dallas, Texas (Sept. 1968).
36. White, A., *Nature*, **214**, 585 (1967).
37. Gupta, M. K., A. B. Metzner, and J. P. Hartnett, *Int. J. Heat Mass Transfer*, **10**, 1211 (1967).
38. McNally, W. A., Ph.D. thesis, Univ. Rhode Island, Kingston (1968).
39. Marrucci, G., and G. Astarita, *Ind. Eng. Chem. Fundamentals*, **6**, 471 (1967).
40. Pruitt, G. T., N. F. Whitsitt, and H. R. Crawford, NASA Contract No. NAS 7-369, The Western Company, Dallas, Texas (1966).
41. Merrill, E. W., K. A. Smith, P. S. Virk, and G. H. Keuroghlian, *AIChE J.*, **15**, 294 (1969).
42. Poreh, M., and V. Paz, *Int. J. Heat Mass Transfer*, **11**, 805 (1968).
43. Wells, S. C., *AIChE J.*, **14**, 406 (1968).
44. Sutey, A. M., and J. G. Knudsen, *Ind. Eng. Chem.*, **6**, 132 (1967).
45. Van Shaw, P., L. P. Reiss, and T. J. Hanratty, *AIChE J.*, **9**, 362 (1963).
46. Van Shaw, P., and T. J. Hanratty, *ibid.*, **10**, 476 (1964).
47. Reiss, L. P., and T. J. Hanratty, *ibid.*, **8**, 245 (1962).

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Kinetics of Slow Thermal Chlorination of Hydrogen in Nickel Tubular Flow Reactors

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The first reliable kinetic data and correlations yet reported were obtained for the thermal reaction of gaseous chlorine and hydrogen over a wide range of operating conditions. Earlier data had been obtained in reactors that result in irreproducible data. The results of the present investigation clarify the reaction sequence that consists of both gas-phase and surface reactions.

The slow thermal chlorination of hydrogen is of considerable interest for at least two reasons. First, the reaction mechanism is similar in many respects to those for the commercially important chlorinations of alkane and aromatic hydrocarbons but without the complicating maze of side reactions present in these latter reactions. Second, the overall reaction sequence involves both homogeneous and heterogeneous reaction steps. Relatively little has been reported on the best methods for describing the kinetics of such reaction systems.

Although the kinetics of the thermal chlorination of hydrogen have been studied by many investigators (*5, 10, 14* to *16, 18-19, 21*), considerable disagreement exists in the literature concerning the proper form of the kinetic equation for this reaction. Models having the form:

$$d(\mathrm{HCl})/dt = k\,(\mathrm{H_2})^a\,(\mathrm{Cl_2})^b\,(\mathrm{HCl})^c \qquad (1)$$

have been proposed. These involve values of a varying from -1 to 2, values of b varying from ½ to 1, and values of c varying from -1 to 0.

Only the models proposed by Kornfeld and Khodschanian (*10*) and Rozlovskii (*18*) were based on theoretical analysis. As will be shown later, a model in which $a = 1$,

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