06 Oct 1971

Recent Developments of Electrochemical Wall Mass Transfer Probes and Their Application to Drag-Reducing Polymers

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Recommended Citation

RECENT DEVELOPMENTS OF ELECTROCHEMICAL WALL MASS TRANSFER PROBES AND THEIR

APPLICATION TO DRAG-REDUCING POLYMERS

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ABSTRACT

Electrochemical mass transfer probes are used to measure the velocity gradient at a wall. Recent advances in their application are reviewed. These include corrections for the time response of the probe, the simultaneous measurement at a number of locations of the two components of the fluctuating velocity gradient and a study of the influence of drag reducing polymers on turbulence. It is found that drag-reducing polymers cause an increase in the scale of flow oriented eddies in the viscous sublayer.

INTRODUCTION

At the 1969 Rolla Symposium on turbulence in liquids, Sirkar and Hanratty[10] described electrochemical techniques that have been developed in this laboratory to study the fluctuating flow in the viscous sublayer. An electrochemical reaction is carried out on the surface of a small electrode mounted flush with the wall under conditions that the reaction is mass transfer controlled. The current flowing in the electrochemical circuit can then be related to the velocity gradient at the wall through the mass balance equation for the reacting species. The time-averaged velocity gradient, $\overline{S}$, and the component of the fluctuating velocity gradient in the direction of the mean flow, s_x, can be measured with a circular electrode or with a rectangular electrode with its long side perpendicular to the direction of mean flow. The difference in the signals from two electrodes in a chevron arrangement gives the component of the fluctuating velocity gradient in a direction transverse to the direction of mean flow, s_z, while the sum gives s_x. In this paper, recent developments in our use of the technique will be summarized and results obtained by applying the technique to drag-reducing fluids will be discussed. More detailed information than is given here can be found in recent theses by Fortuna[3] and Eckelman.[1]

RESULTS AND DISCUSSION

A. Time Response of the Probe

The current flowing in the electrochemical circuit, I, is related to the transfer coefficient, K, characterizing the mass transfer to an electrode surface of area, A, by the equation:

$$I = \frac{K(C_B - C_W) A}{n_e F} \qquad (1)$$

where n_e is the number of electrons involved in the reaction, F is Faraday's constant, C_B is the bulk concentration and C_W is the concentration at the surface of the electrode. Since the reaction is carried out at fast enough rates that it is mass transfer controlled, $C_W = 0$.

The mass balance equation for a rectangular electrode with its long side perpendicular to the direction of mean flow is given by:[10]

$$\frac{\partial C}{\partial t} + S_x y \frac{\partial C}{\partial y} = D \frac{\partial^2 C}{\partial y^2} \qquad (2)$$

where C is the concentration of the reacting species at a distance y from the wall. This equation is to be solved with C = 0 at y = 0 and with C = C_B at

large y. If one makes a pseudo-steady state approximation and neglects $\frac{\partial C}{\partial t}$, the following relation between the mass transfer coefficient and the velocity gradient is obtained:

$$\frac{(\overline{K} + k)\, L}{D} = 0.807 \left[\frac{(\overline{S}_x + s_x)\, L^2}{D} \right]^{1/3} \qquad (3)$$

Where D is the diffusion coefficient and L is the length of the electrode. If $\frac{s_x}{\overline{S}_x}$ is small enough, Eq. 3 can be simplified to give:

$$\frac{(\overline{s_x^2})^{1/2}}{\overline{S}_x} = 3 \frac{(\overline{k^2})^{1/2}}{\overline{K}} \qquad (4)$$

Eq. 4 can be in error because of the neglect of the $\frac{\partial C}{\partial t}$ term in Eq. 2 if the signal has a significant portion of its energy in the high frequency range. Mitchell and Hanratty[9] suggested that the frequency response of the wall electrode may be taken into account by solving the linearized form of Eq. 2,

$$\frac{\partial c}{\partial t} + \overline{S}_x y \frac{\partial c}{\partial y} + s_x y \frac{\partial \overline{C}}{\partial y} = D \frac{\partial^2 c}{\partial y^2} \qquad (5)$$

and presented results for a limited frequency range. Recently, Fortuna[3,4] has improved the numerical methods employed by Mitchell and Hanratty and has presented results which are valid for all frequencies. The spectral density function for s_x is related to the spectral density function for k through the equation:

$$W_{s_x} = 9 \frac{\overline{S_x^2}}{\overline{K^2}} \frac{W_k}{A^2} \qquad (6)$$

For low frequencies, A = 1 and for high frequencies, A can be obtained by methods outlined by Lighthill.[7] Finite difference solutions to Eq. 5 can be used to obtain results for intermediate frequencies. The results of these calculations are shown in Figure 1, where L^+ signifies the length of the electrode made dimensionless with respect to the friction velocity, u^*, and the kinematic viscosity, ν. The dimensionless frequency, ω^*, is defined by the equation:

$$\omega^* = \frac{\omega \nu}{u^{*2}} N^{1/3} \qquad (7)$$

where N is the Schmidt number. Of particular interest is the influence of the Schmidt number or Prandtl number on the frequency response. Mass transfer probes have involved systems with Schmidt numbers 1000-3000, while a thermal probe in water would be characterized by a Prandtl number of 5. From Figure 1, we conclude that thermal probes have much better frequency response than mass transfer probes. This arises because probes operating with fluids of smaller Schmidt number or Prandtl number have thicker scalar boundary layers and, therefore, see larger velocities

B. Multiprobe Measurements

Current interest in the structure of turbulence has led to the development of techniques to measure simultaneously the components s_x and s_z at ten different locations on a pipe wall. Sirkar and Hanratty[10] have shown that the
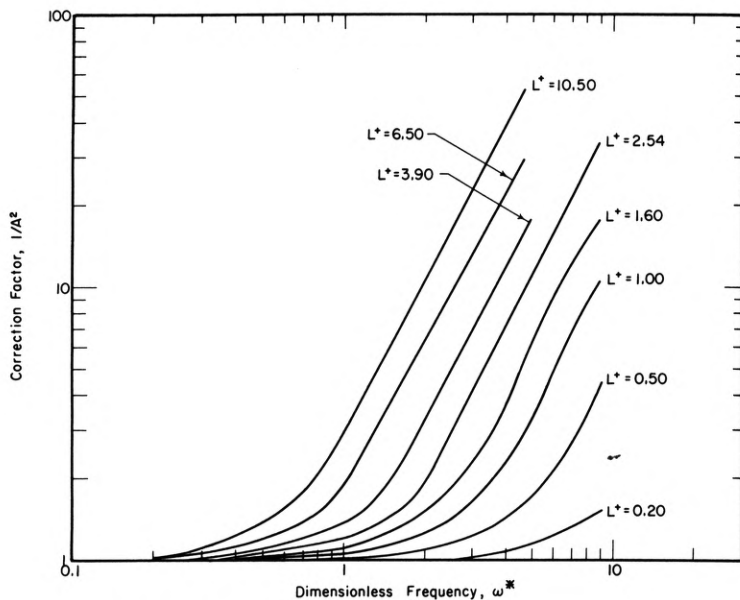
Figure 1 – Correction Factor for Pseudo-Steady State Solution

electrode arrangement shown in Figure 2 can be used to measure s_x and s_z provided:
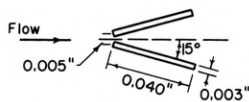
$$\frac{|s_z| \cos \phi}{|\overline{S} + s_x|} < 1$$

Figure 2 – Chevron Arrangement of Electrodes

The difference of the signals from the two electrodes gives s_z since:

$$\frac{K_1 - K_2}{\overline{K}} = \frac{2}{3} \frac{s_z}{S} \left(\frac{\cot \phi - \frac{2L \cot^2 \phi}{5W}}{1 + \frac{L}{5W} \cot \phi} \right) \qquad (8)$$

while the sum gives s_x since:

$$\frac{K_1 + K_2}{\overline{K}} = \frac{2}{3} \frac{s_x}{S} \qquad (9)$$

A portion of the multiprobe arrangement used by Eckelman is shown in Figure 3. The slanted electrodes were constructed in an external plexiglas block which was later glued into the test section. A 1-1/2 inch x 1-3/4 inch x 1/2 inch block was milled so that a 1/4 inch x 1/4 inch strip extended from the center of one side and a trough existed on the reverse side. Twenty 0.013 inch holes separated by a distance of 0.036 inches were drilled in the trough through the strip. Slots 0.005 inches wide by 1/8 inch deep were cut through the 1/4 inch strip, and 1/4 inch x 1/8 inch x 0.003 inch platinum tabs with a 32 gauge insulated copper wire spot welded to them were glued into the slots. After drying for 24 hours, the electrodes were milled to size. After sizing the strip was enlarged to 1/4 inch wide by gluing in plexiglas strips, and 0.013 inch holes were drilled between the parallel electrodes. Then, the process of slotting holes, gluing in platinum tabs, and sizing electrodes was repeated to complete the construction. Finally, the surface was milled to the curvature of an 8 inch pipe, the excess plexiglas was cut away, and the plug was inserted into the pipe wall. After three such plugs were inserted
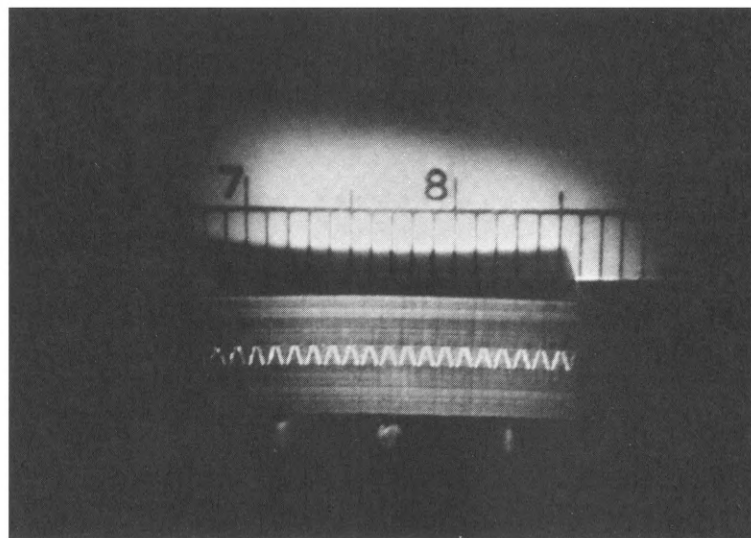

Figure 3 – A Portion of the Multiprobe Arrangement

side by side into the pipe wall, the electrodes were sanded and polished with emery paper.

Circuits for the addition and subtraction are shown in Figure 4. Ten such circuits have been used by Eckelman[2] to measure s_x and s_z from five different locations. Lee[6] is currently using twenty circuits for measurements at ten locations. The signals from the electrodes are either recorded on a tape or fed directly to an IBM 1800 computer.
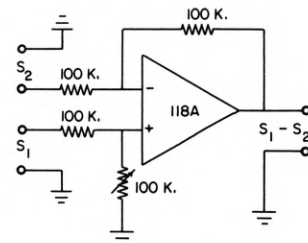
a) Transverse Fluctuations
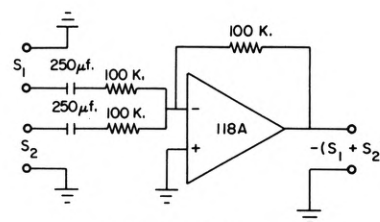
b) Axial Fluctuations

Figure 4 – Simultaneous Measurement of Transverse and Axial Fluctuations From a V Electrode

C. Studies of Drag Reduction

There is considerable evidence to suggest that turbulent drag-reduction can be associated with changes in the turbulence in the viscous sublayer. Therefore, electrochemical wall mass transfer probes offer an opportunity to obtain an understanding of the influence of drag-reducing polymers on a turbulent field. This is particularly true because the probes are mounted flush with the wall and, therefore, do not interfere with the flow field.

Fortuna has recently carried out such studies in a 1 inch pipe[3,5]. Difficulties were encountered in using electrochemical techniques in drag reducing solutions because the hydroxl ions in the electrolyte accelerated degradation and because drag-reduction occurs at high enough friction velocities that the time response of the electrode must be taken into account. Measurements were

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made of $\overline{s}_x$, $(\overline{s_x^2})^{1/2}$, $(\overline{s_z^2})^{1/2}$, the frequency spectra for s_x and s_z and correlation coefficients for s_x.

The time-averaged velocity gradient is related to the time-averaged wall stress by Newton's law of viscosity. The view is taken that comparisons of the turbulence structure with and without polymers should be made at the same friction velocity. Therefore, all turbulence measurements have been normalized with respect to wall parameters. On this basis, we find that the changes in the intensity of s_x and in the shape of the spectral density functions for s_x and s_z are not comparable to the decrease in pressure drop caused by the addition of polymer. The root-mean-squared value of s_z shows a significant decrease with an increase in drag reduction, but the most spectacular change in turbulence structure seems to be associated with an increase in the scale of the turbulence.

Measurements of the correlation of s_x in the z-direction show negative values of the correlation coefficient at large values of z. Fortuna[3] has associated the distance between the zeros of the correlation coefficient with the lateral length, λ, of the flow oriented eddies described by Kline, et al.[8]. By using this type of reasoning, a given amount of drag-reduction can be associated with an increase in λ. Recent simultaneous measurements of s_x at ten different locations on the wall by Eckelman[2] have confirmed this interpretation. If the burst frequency of the flow oriented eddies defined by Corino and Brodkey[1] from their visual studies is a characteristic of the frequency spectrum of the fluctuating flow, then we would not expect it to be different from that for a Newtonian fluid if it is normalized with wall parameters.

By using a simplified model for the wall eddies such as has been used by Sirkar and Hanratty[11] to interpret wall mass transfer and the equations for a Newtonian fluid, it can be shown that the magnitude of the decrease in pressure is consistent with the estimated increases in λ obtained from correlation measurements.

Because of the observation that the time-averaged wall stress is related to the time-averaged velocity gradient by Newton's law of viscosity, we find the notion of an anisotropic viscosity to be particularly attractive as an interpretation of the influence of drag-reducing polymers on the rheological properties of the solution. An increase in λ can then be interpreted as resulting from larger viscous resistance to flows in the z-direction than to flows in the x-direction.

ACKNOWLEDGEMENT

SYMBOLS

A	area of test electrode
A	coefficient defined by Eq. 5
C	concentration of reacting species
C_B	bulk concentration
C_w	concentration at the wall
c	concentration fluctuations
D	diffusion coefficient
F	Faraday's constant
I	electric current
K	mass transfer coefficient
k	fluctuating mass transfer coefficient
L	electrode length
L^+	*equal to* $L\,u^*/\nu$

n_e	number of electrons involved in the reaction
N	Schmidt number or Prandtl number
S_x	x-component of the velocity gradient at the wall
s_x	x-component of the fluctuating velocity gradient at the wall
s_z	z-component of the fluctuating velocity gradient at the wall
t	time
u^*	friction velocity
W_k	spectral density function for k
W_{s_x}	spectral density function for s_x
x	coordinate in the direction of mean flow
y	coordinate perpendicular to the wall
z	coordinate in the transverse direction

Greek Symbols

λ	wave length of flow oriented eddies
ν	kinematic viscosity
ϕ	angle which slant probe makes with x-axis
ω	frequency, radians per second
ω^*	dimensionless frequency defined by Equation 6

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DISCUSSION

W. G. TIEDERMAN (Oklahoma State): Would you comment further upon the differences and similarities between the results of our visual work and your electro-chemical technique?

HANRATTY: Your question and your previous comments indicate that your visual experiments tentatively suggest no change in scale and a decrease in bursting frequency when comparisons are made at constant flow. If the frequency of the bursts that you see are a parameter of your frequency spectra this would seem to suggest that there is agreement between your results and ours. We get lower frequency signals by the addition of drag reducing polymers, keeping flow constant. If you make your comparison at the same friction velocity then the difference in bursting frequency with the addition of polymer shouldn't be as great. However, there might be some disagreement between your and our eddy scales. We find that drag reducing polymers cause a spectacular increase in the eddy scale as is suggested from our correlation measurements or from our measurements of the instantaneous transverse velocity component in a

number of different places. We're finding that λ^+ can increase from 100 to 400. This increase would be greater if the comparison was made at the same average velocity. Therefore, the effect of polymers on the scale would appear even more spectacular if we didn't normalize with respect to wall parameters. I don't understand this difference between your scale measurements and ours.

A. FABULA (Naval Undersea R&D Center): Would the authors care to offer any comments on various theories of the basic mechanism of polymer friction reduction in view of their observations of turbulence structure changes?

HANRATTY: The model that I presented would suggest that one ask why the addition of the polymers causes an increase in the wave length of the characteristic eddies. Is the addition directly affecting the eddies or is it affecting something else in the turbulence which in turn affects the eddy size? I don't know. There are a number of possible explanations for this. One, which was used by the MIT group, is a non-isotropic viscosity. The transverse fluctuations might see a more viscous resistance than the fluctuations in the mean flow direction. Accordingly, the viscosity I'm using to normalize the wave lengths is not the correct one. If I used a different one I'd get 100 back again.

R. J. HANSEN (Naval Research Laboratory): With regard to the suggestion you just made, I believe that the optical studies of Cottrell and Merrill of the conformation of polymer molecules in shear flows may be relevant. This work indicated that the polymer molecules were not greatly elongated and that any anisotropic viscosity effect was therefore small. Would you care to comment on this?

HANRATTY: I'm not sure that the experiments that you've quoted were done at high enough shear rates to say that they would exclude this as a possible mechanism. They did work in a Couette viscometer and looked at the influence of the shear field on the elongation of polymer molecules, but this was for much smaller shear fields than you have in turbulent flows under drag reducing conditions.

H. C. HERSHEY (Ohio State University): I didn't see any intermittency in your results as was observed by Seyer and Metzner.

HANRATTY: We see no evidence of intermittency at the wall. Maybe one has to use a more sophisticated way of processing our electrode signals to see it, if it exists.

S. KLINE (Stanford): Can you say anything more than you already have about what happens to the time scales. You were fairly clear about the length scales, but I didn't get a very clear picture about the time scales.

HANRATTY: I guess we really haven't tried to come up with parameters like bursting times or characteristic times. The only thing we've done so far is to look at the spectra and these seem to come together if you normalize with wall parameters. This is not exact. I don't think one can infer from this that if you normalize your bursting time with wall parameters it is going to be exactly the same for drag-reducing and for Newtonian fluids. However, the differences will probably not be as spectacular as the spatial differences that we've observed.

V. GOLDSCHMIDT (Purdue): You said that you were not pleased by the results. You were going to try to account for the du/dt term whose elimination you felt brought some error. What are you hoping to account for, what extension will the du/dt inclusion bring, and how will that inclusion be made?

HANRATTY: What bothers me is that we threw away a term that shouldn't have been thrown away. The derivative of u with respect to time is not a negligible number over maybe 50% of the spectra. There are other problems in implementing the model. There is a lot of latitude in the selection of the parameters. We used λ^+ of a hundred. It could be 70 or it could be 125. Also what is the influence from a distribution of wave lengths. Another problem is that we assumed 100 percent of the turbulence is associated with large eddies. This is probably not correct. I don't know how to include all these things in the model. If we stay very simple, along the lines that I presented, you get pretty good results.

JOHNSON: In 1966 we made some flush-mounted hot-film measurements of polymer injection in boundary layers (reported in Vol. 2 of the Journal of Hydronautics). We measured a predominant shift to a much larger eddy structure, and a decrease in the higher frequency eddies consistent with your measurements. We discussed the influence of the polymer on vortex stretching in terms of the inertial character of turbulence rather than the viscoelastic properties of higher concentrations of the polymer. We suggested that for a given amount of vortex stretching, the long chain polymers decrease the rotational acceleration of the vortices present in the boundary layer. This would in turn decrease the rate of turbulence energy transfer by the cascade process, and result in less energy deficit to be extracted from the mean flow. Our phenomenological explanation of drag reduction goes counter to some of the current measurements that are being reported, however. Visual burst observations show that energy doesn't just go from large eddies to small eddies. Some of it appears to go from small eddies to large eddies in spite of the quatrain about "big whirls form little whirls." So the cascade theory may be a misleading concept if we are attempting to explain the production of turbulence. The other problem in interpreting the switch to a predominantly large eddy structure in polymer flows is that the reported measurements of pressure fluctuations don't follow this trend. Dr. Richard Nadolink gave a presentation recently in which he showed an opposite shift towards the higher frequencies. And so the interaction between pressure and velocity fluctuations in polymer additives is a confused issue at this time.