The Influence of Molecular Agglomerates on the Drag Reducing Properties of Polyethylene Oxide Solutions

H.D. ELLIS

Lecturer, Queensland Institute of Technology

I. COWLING

Senior Tutor, Queensland Institute of Technology

and

R.J. NORTON

Lecturer, Queensland Institute of Technology

SUMMARY   Experiments aimed at examining the drag reducing behaviour of aqueous solutions of high molecular weight polyethylene oxide which have been allowed to diffuse through porous barriers into water are reported.   While there is some evidence to suggest that a change in behaviour may occur, no clear picture emerges of what occurs upon diffusion.   In particular, the "stringy" or pituitous nature of the polymer solution unexpectedly persists after the solution is diffused through a filter of submicron pore size. Future extensions to the work reported are suggested.

1   INTRODUCTION

The loss of energy experienced by fluids in motion, or by objects moving through fluids, is an accepted fact of life.   Drag reduction is the term most widely used to describe a reduction in this energy loss.

Since the early work of Blatch (1906) and Toms (1948) much work has been carried out on drag reduction using additives to the fluid.   Such additives are normally very high molecular weight polymers, though fibres have been used successfully (Bobkowicz and Gauvin, 1965 and Ellis, 1970). Reviews of the drag reduction field have been given by Lumley (1969), Hoyt (1972), Patterson, Zakin and Rodriguez (1969), Gadd (1966 and 1967) and Virk (1975).

While just a few parts per million of polymer are needed to give very large drag reductions (around 80%), polymers readily lose their effectiveness, degradation being caused by shear stress or oxidation (Barnard and Sellin, 1972, Paterson and Abernathy, 1970, Brennen and Gadd, 1967, Ting and Little, 1973 and Kim et al, 1974).

Some work has been carried out on the role played by molecular agglomerates in drag reduction. Brennen and Gadd (1967) obtained results with polymer solutions which showed that apparent viscosity and pitot tube pressure anomaly changed with the age of the polymer, while drag reduction did not.   Investigations of the variation of volume concentration and size of molecular agglomerates with age using the pitot tube anomaly have been reported by Kalashnikov and Kudin (1973). One of us (Ellis, 1970) has previously reported on anomalous results obtained with polymer solutions subjected to shear treatment.   In this experiment, Polyox WSR 301 solution was tested for drag reduction in large (1.43 cm diameter) and small (0.115 cm diameter) tubes.   Following shear treatment repeats of the measurements showed little change in drag reduction in the small tube, while the drag reduction in the large tube disappeared. This result suggested that perhaps molecular agglomerates were responsible for drag reduction where the scale of turbulence was large, and that the shear treatment had disentangled the agglomerates without damaging the individual molecules.

Cox, Dunlop and North (1974) investigated the time dependence of drag reduction in solutions of poly(ethylene oxide) and polyacrylamide.   Their result suggested that molecular agglomerates may play an important role in drag reduction.

The difficulty in delving further into the role of agglomerates is that it is almost impossible to obtain polymer solutions in which the agglomerates have been disentangled, and in which the molecules have not been damaged by scission.   Attempts to use shear stress as a disentangling tool must leave some doubt that either agglomerates still exist, or that the molecules have been damaged.   One possible method is to allow the polymer solution to diffuse through a barrier with holes small enough to prevent the passage of agglomerates, but large enough to allow single polymer molecules to pass.

This paper reports on preliminary attempts to obtain non-agglomerate solutions by such a method, together with the results of tests to determine differences between diffused and undiffused solutions.

2   EXPERIMENTAL PROCEDURES

In broad terms, the experimental plan was to diffuse polymer solutions through a barrier and characterise the diffusant in the large scale drag reduction test apparatus (Appendix B).

Initially, the small scale test apparatus (Appendix A) and large scale test apparatus (Appendix B) were characterised using solutions of Polyox WSR 301 from the polymer batch to be used in the experiment. Solutions (of the order of 1-2% and a volume of 5 litres) were prepared from a suspension of the Polyox powder in a small quantity of methylated spirits, by adding water to make up to the final concentration very rapidly while stirring. Stirring was continued for 5 minutes, then the solution was allowed to stand, with intermittent stirring, for a day before use.   The methylated spirits remaining in the solution prevented oxidation.   These solutions are highly viscous and appear to be stable almost indefinitely.

The small scale test apparatus was characterised for this batch of polymer solution by using it to measure drag reduction as a function of polymer concentration.   The results are shown in Figure 1.
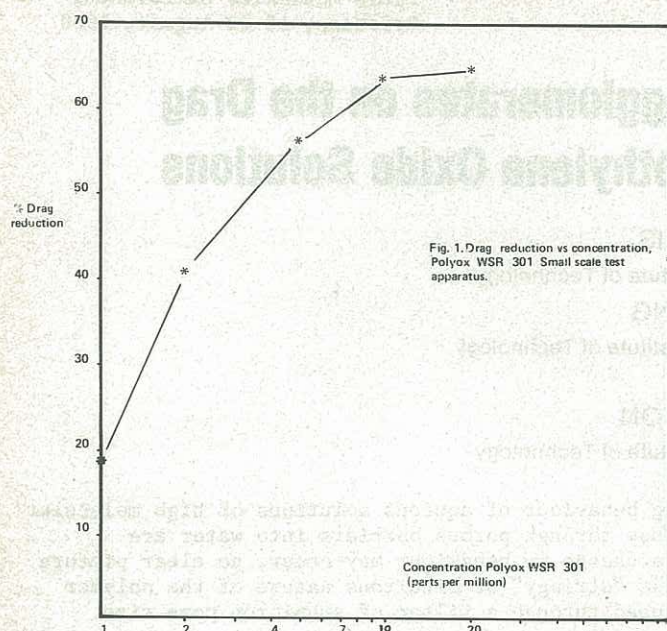
Figure 1 — Small apparatus characterisation

Figure 2 shows some characterisation results for the large scale test apparatus using the Polyox WSR 301 solution used in the diffusion experiments. Reynold's number is denoted Re, and f is used to symbolise the Fanning friction factor.
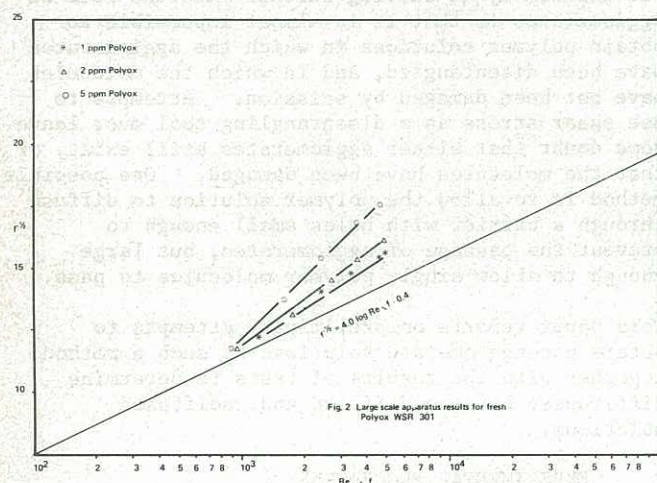

Figure 2 — Large apparatus results – fresh Polyox WSR 301

Rectangular glass tanks measuring 25 x 14 x 14 cm were used as diffusion vessels, with the diffusion barrier supported by a suitable frame, sealed to the interior of the tank in a longitudinal upright position, dividing the tank into two equal volumes. To prevent pressure-head flow through the barrier while preparing the tanks for diffusion, two large syringes were used in synchronism, one feeding water to one side of the barrier, the other feeding polymer solution to the other side. In some cases the tanks were placed in a warm water bath to speed the diffusion process. Barriers used were –

100 mesh gauze, hole size approximately 170 μm
400 mesh gauze, hole size approximately 38 μm
Whatman No. 3 filter paper (retains approximately 5 μm)
Millipore filter, hole size 1.2 μm
Millipore filter, hole size 0.22 μm

For the last three, the diffusion tanks were duplicated and diffusion was carried out at 20°C and 40°C.

The tanks were sealed to prevent evaporation and left to stand to allow diffusion to proceed. The diffusant was examined periodically for polymer threads by dipping an object into the surface and withdrawing while observing for the characteristic stringiness of concentrated polymer solutions. When diffusion had proceeded sufficiently, a sample of the diffusant was tested by progressive dilution in the small scale test apparatus to establish an approximate equivalent concentration using the results of Figure 1. This was then used to calculate the quantity of diffusant needed to carry out a large scale apparatus test at an equivalent concentration of 5 parts per million.

In addition, one part of the concentrated solution batch was subjected to shear thinning treatment with a high velocity mechanical stirrer and was tested and characterised in similar fashion.

3   RESULTS AND DISCUSSION OF RESULTS

Prior to this work, investigation had established that vacuum filtration of concentrated Polyox solutions through filter paper had little effect on the "stringy" nature of the solution. Since the stringiness of the solution is thought to be related to the presence of molecular agglomerates, it seemed reasonable to assume that, due to the forced flow of solution through the filters, the agglomerates had deformed elastically and thus passed through. It was anticipated that by using diffusion where the flow of material through the barrier was very slow, the agglomerates would not elongate, and would thus be retained, while individual disentangled molecules would diffuse readily.

In fact, the diffusant from coarse mesh experiments exhibited stringiness after less than a day standing at 20°C, and all subsequent barriers were ineffective in preventing the appearance of stringiness in the diffusant, though in the case of the very small hole barriers, several weeks elapsed before stringiness became evident. As expected, elevating the solution temperature to 40°C merely accelerated the process. All diffusion barriers showed an osmotic effect, with the fluid on the 'polymer' side being as much as 40 mm higher than the fluid on the 'water' side. This effect showed a peak with the osmotic pressure decreasing with time after reaching a maximum.

Figure 3 shows a summary of the results obtained using the large scale drag reduction test apparatus. The line shown for the 5 μm filter is typical of
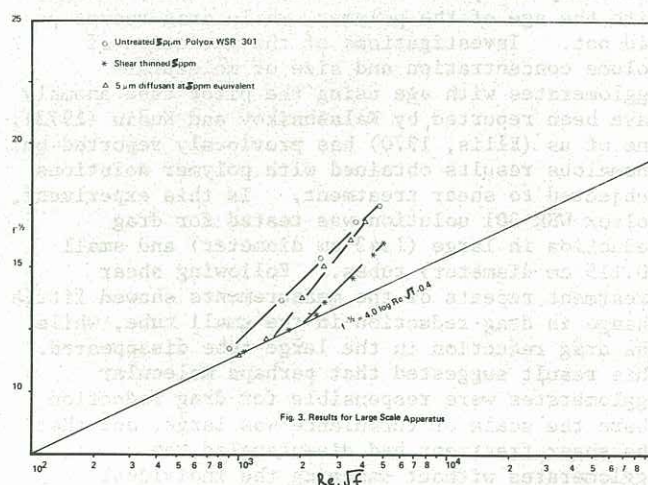

Figure 3 — Large apparatus results – treated Polyox WSR 301

the data from other diffusants. The curve for the shear treated polymer is consistent with decreased molecular weight (Virk, 1975).

It seemed reasonable to suppose that the process of diffusion would reduce the polymer agglomerate size. This supposition is not inconsistent with the results obtained. However, the appearance of pituity (stringiness) in the diffusant was a very unexpected feature, and needs to be looked at closely.

4 CONCLUSION

The results obtained suggest that there may be a change in characteristic of the polymer solution used following diffusion. This change in characteristic is unlikely to be due to a decrease in molecular weight, though the use of a control solution would remove any doubt.

The principal result of this work to date is that very small pore filters do not prevent the appearance of stringiness in diffused Polyox solution. There are two possible explanations for this observation, assuming that stringiness is linked with the presence of molecular agglomerates. Either the agglomerates pass through the barrier intact, or are reformed after the individual molecules pass through.

Thus, the situation seems more complicated than was anticipated, and to progress beyond the inconclusive results obtained here will require more extensive investigation in several areas. These areas may be listed as follows:-

(a) Testing of diffusants in the large scale apparatus at higher concentrations.
(b) Examination of how "stringiness" changes with time for the diffusants and diffuser.
(c) Elimination of possible osmotic pressure head effects.
(d) Examination of the time dependence of the diffusant drag characteristic.

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APPENDIX A

SMALL SCALE DRAG REDUCTION MEASUREMENT APPARATUS

In this apparatus, the fluid under test is forced from a syringe by a weight-driven piston. Microswitches are operated by the downward movement of the weight and are connected to a timer which displays the time taken for a given volume of fluid to be forced through the tube.

Several readings for the fluid under test, and for water at the same temperature, are used to give a percentage drag reduction with standard deviation.
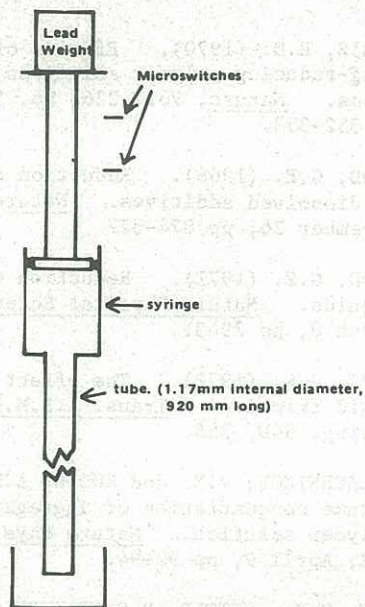
Figure 4   Small scale apparatus

The drag reduction is defined as

$$\left(1 - \left(\frac{T_p}{T_w}\right)^2\right) \times 100\%$$

where T_p is the mean ejection time for the test
          fluid, and
   T_w is the mean time for water.

Repeatability of about 2% is achieved, so that a drag reduction of 50% is normally quoted as $(50 \pm 1)\%$.

APPENDIX B

LARGE SCALE DRAG REDUCTION MEASUREMENT APPARATUS

In essence, the large scale apparatus is gravity fed, using a 300 litre parallel sided supply tank, 23.8 mm internal diameter flexible supply tubing and 19.8 mm internal diameter metal tube for the test section.   A throttle is used to obtain various flow rates.   The unusual feature of the apparatus is the means for obtaining flow rates. A large diameter flat bottomed weighted float is attached by a lightweight chain to a tensioning counterbalance.   The chain drives a multi-turn potentiometer via a suitable diameter gear wheel. The potentiometer is fed from a constant voltage source, and the output voltage is sampled and displayed on a latched digital read-out at predetermined time intervals.   The time interval is selectable by numeric thumb-wheels from 1 to 99 seconds, and is derived from a crystal controlled oscillator.   Initial investigation showed that, contrary to expectation, the change in output voltage from the potentiometer was not proportional to the change in volume of fluid contained in the tank.   Though the departure from linearity was slight, it was significant, and a calibration was undertaken.   The calibration gave data from which a curve fitting computer programme yielded a cubic function which adequately approximated the relationship between digital readout and volume contained by the tank.

In use, flow rate is obtained by volume subtraction over a known time interval, and pressure gradient from differential manometer readings.   Data are obtained for several different flow rates from a single tank full of fluid.   From the flow rate, pressure gradients and fluid temperature, friction factor and Reynolds number are calculated using the formulae

$$f = \frac{\pi^2}{32} \frac{g\, d^5}{\ell} \cdot \frac{\Delta h}{Q^2} \quad \text{and} \quad R_e = \frac{4\rho Q}{\pi \eta\, d}$$

where $g = 9.79 \text{ m s}^{-2}$,
   d is the pipe diameter,
  Δh is the differential water manometer height
      difference,
   ℓ is the distance between pressure taps on the
      test pipe,
   Q is the volumetric flow rate,
   ρ is the density of the fluid, and
   η is the viscosity of the solvent fluid.

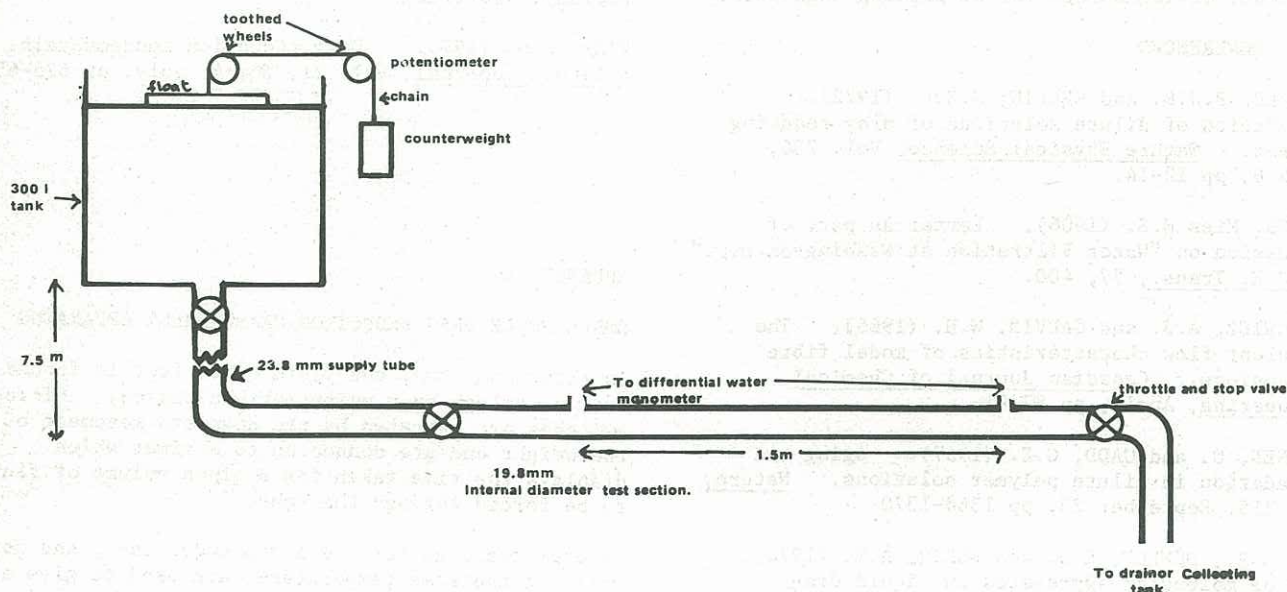Repeatability is about 2% in this apparatus, and periodic checks using water show excellent agreement with theoretical values for all turbulent Reynolds numbers up to the highest used.

Figure 5   Large scale apparatus