 DOI: 10.1002/masy.200651336

Development of a Method to Evaluate the Performance of Aqueous Polymer Solutions as Drag Reduction Agents in Bench Scale

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Summary: This work describes a method to evaluate, in reduced scale, the performance of polymer samples as drag reduction agents in aqueous solutions. To measure the pressure drop in a turbulent regime, a specially adapted capillary viscosimeter was used, with reduced dimensions adapted to produce the desired regime and adequate pressure measurement points. To verify the technique's reliability, samples of polyacrylamide were synthesized with different molar masses, by varying the quantity of the polymerization initiator. The molar masses obtained were determined by size exclusion chromatography (SEC). The efficiency of the polymer as a drag reducer, as expected, increased as the molar mass increased, which validates the use of this method to study the drag reduction properties of polymer materials in aqueous solutions.

Keywords: drag reduction; polyacrylamide; polymer solution; pressure drop; turbulent regime

Introduction

The phenomenon of drag reduction in turbulent flows due to the presence of certain flow modifiers has been the subject of many studies in the past forty years. The investigation of how they work is very important due to their potential application in engineering, since drag reduction of up to 50% can be obtained through addition of just a few parts per million by weight of polymeric additives, notably linear polymers with high molar weight or low fiber concentration (on the order of 1%). The drag reduction can be manifested as a lower coefficient of friction, a decrease in pressure drop per unit of pipe length or a reduction in the energy required to pump a fluid or propel an object through a fluid.[1–4]

The British chemist B. A. Toms[1] (1949) was the first to publish data on drag reduction (the phenomenon is also known as the Toms Effect), reporting lower friction factors than expected for diluted solutions of poly(methyl metacrylate) in monochlorobenzene under turbulent flow through pipelines. Mysels[4] (1949) observed a similar effect for gasoline thickened with aluminum soaps.

In 1959, results of research on the same subject were published simultaneously.[5,6] Both works described lower friction factors for diluted polymer solutions. Shortly thereafter, researchers in the oil industry reported friction reduction in suspensions of guar gum, sand and water, used in fracturing oil wells.[7,8] The works of Crawford[9] and Savins[10] attracted atten-

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tion from the American Navy, whose scientists made significant contributions. For example, the work of Fabula *et al.*[13] is given credit for the discovery of the drag reduction properties of poly(ethylene oxide), the most studied and commercially used drag reduction agent.

Despite the many studies conducted over the years, the phenomenon is still not fully understood, and the chemical, mechanical and hydrodynamic aspects of drag reduction still need further study. The large number of recent publications in this area attests to the fact that drag reduction continues to be an important research topic.[14–24]

There are reports in the literature of various solvent/additive systems that have drag reduction properties, including diluted solutions of natural or synthetic polymers with high molar mass,[1–12] surfactants and micellar systems,[21,25] suspensions of insoluble particles such as fine grains or fibers[26,27] and polymer solutions mixed with soaps or fibers.[28–32]

In general, any soluble polymer that has a sufficiently high molar mass (greater than 1×10^5), or that is able to form large aggregates, can be effective in reducing friction in a turbulent regime. Linear or branched polymers, with rigid or flexible chains, homopolymers or copolymers, isolated or aggregated molecules and polymers with high or low affinity for the solvent have all been shown effective in reducing drag. However, the relation between the drag reduction efficiency and chemical composition parameters and interactions (polymer/polymer and polymer/solvent) are still not well understood. Studies of drag reduction generally concentrate more on the structure of the turbulence than on the nature of the additives, leaving many questions unanswered on the role of the polymer and the solvent in the process.[33]

In order to assess the influence of the structure and physical-chemical properties of polymers on drag reduction, it is necessary to synthesize, characterize and evaluate the performance of families of polymers obtained in bench scale. But since in the great majority of cases the drag reduction tests are conducted in systems that require a large volume of solution, preliminary tests with polymer samples synthesized in bench scale are not feasible. This work presents a methodology to evaluate drag reduction that only requires small volumes of solution, and consequently, small amounts of polymer. To verify the accuracy of this technique, samples of polyacrylamide were synthesized with different molar masses, by varying the quantity of the polymerization initiator.

Methodology

Synthesis of the Polyacrylamide

The polyacrylamide was synthesized in a 250-mL round-bottom flask coupled to a reflux condenser, under heating. Acrylamide and distilled water were kept under agitation for 30 minutes under a nitrogen flow. Afterward, hydrogen peroxide (initiator) was added and the reaction was conducted for 2 hours. Table 1 presents the reaction conditions for each of the polyacrylamide samples.

The polymer formed—soluble in water—was precipitated in methanol and dried in a vacuum oven at 50 °C for 24 hours. The purification was done by solubilization of the polymer in distilled water, reprecipitation in methanol and again drying in a vacuum oven at 50 °C for 24 hours.

Table 1.
Reaction conditions to obtain the polyacrylamide samples.

Polymer	H_2O_2	Solid content	T
	(%wt/wt)*	(%wt/v)	(°C)
PAAm 1	1.3	50	70
PAAm 2	1.6	10	65
PAAm 3	1.0	10	65
PAAm 4	1.3	10	65
PAAm 5	0.5	10	65

* Concentration of the initiator in relation to the acrylamide mass.

Determining the Molar Mass

To evaluate the mean molar number and weighted mean molar mass of the polyacrylamide samples, along with the polydispersion, we used a Waters model 600C chromatograph, with Polysep-GFC-P columns (Polysep 1000, 4000 and 6000). We obtained the calibration curve through patterns of poli(ethylene glycol) and pullulan from Phenomenex. The mobile phase used was an aqueous solution of sodium azide (NaN_3) at a concentration of 1.0 ppm.

Pressure Drop Test

The capillary viscosimeter, adapted to obtain data in turbulent flows of polymeric solutions, is shown in Figure 1.

The device has a hose (1), specially designed to withstand high pressures, connected to a compressed air line. This hose has a valve (2) that serves to control the pressure inside the device's chamber (5). The pressure is also monitored by a pressure gauge (3) placed at the outlet of the valve (2). Once the working pressure is established inside the chamber (5), another valve (7) is opened permitting the fluid to flow through the capillary (9) and escape the system through the expander (10). The fluid flow rate is determined by placing a 100-mL test tube at the expander outlet and using a stopwatch to time how long it takes it to fill. The pressure drop is read directly on the pressure gauge (8). Once all the solution has left the device, the system's pressure is alleviated by manipulating the valves (2) and (4), and the chamber can then be opened by taking off the screw-on lid (6), so the system can once again be loaded with the fluid or cleaned by circulating water.

We evaluated each polymer solution twice, at a concentration of 0.1 g/L. We set the Reynolds number at 7000 to calculate the pressure drop and percentage of drag reduction, computing the latter for each solution in relation to the pressure drop of pure water.

We used the following definition for the Reynolds number (Re) to evaluate the flow regime of the pseudoplastic solutions:

$$\mathrm{Re} = \frac{D^n u^{2-n} \rho}{K(8)^{n-1}} \qquad (1)$$

where u is the average velocity, ρ is the density, D is the diameter of the capillary tube, and n and K are rheologic parameters.

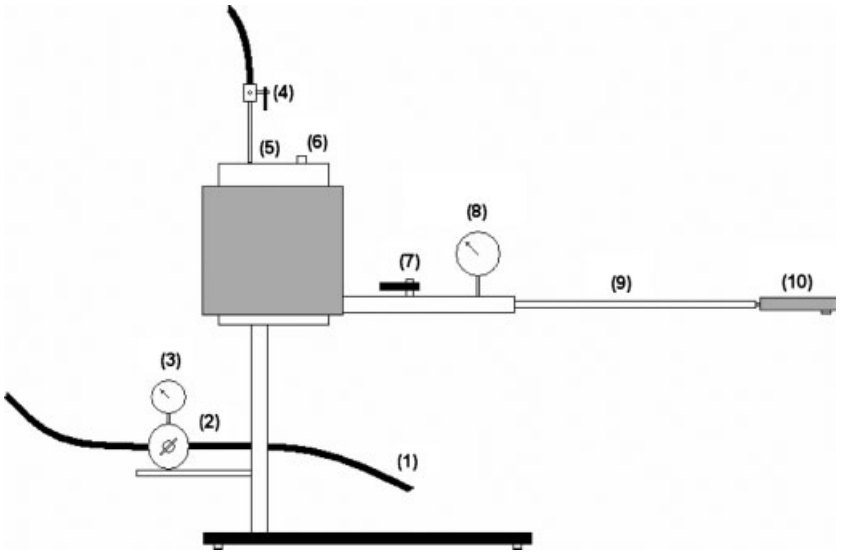

Figure 1.
Schematic representation of the capillary viscosimeter.

Determining the Rheologic Parameters K and n

We obtained the parameters K and n by adjusting a power law (Equation 2) to the viscosity measures under continuous flow (1000–5000 s^{-1}).

$$\eta = K\gamma^{1-n} \quad (2)$$

where η is the viscosity and γ is the shear rate.

Results and Discussion

Determining the Molar Mass

Table 2 shows the mean numeric and weighted mean molar mass, along with the polydispersion, obtained for each of the polyacrylamide samples synthesized.

From Table 2 it can be seen that, as desired, polymer samples were obtained with the same structure and varied molar masses. Samples PAAm 1 and PAAm 2 had approximately the same mean numeric molar mass. The polydispersion (M_w/M_n,) did not vary greatly from sample to sample, fluctuating around 3.5.

Assembling the System to Determine the Pressure Drop

Due to the small amount of polymer samples synthesized in laboratories, we had to develop a reduced-scale device to evaluate the drag reduction. To do this we used a capillary viscosimeter, depicted in Figure 1. We chose the capillary length so as to have a length/diameter (L/D) ratio greater than 115. Since the diameter was approximately 1 mm, this meant choosing a length of 0.41 cm, determined by direct measurement with a tape measure. Once we established the capillary's dimensions, we fabricated it of steel.

Since the capillary's diameter should not be totally uniform along its length, which hinders its direct measurement, we chose to determine the equivalent diameter indirectly through a test with standard oil (mineral oil – OP 10 IPT 78) in a laminar regime. We applied pressures of 10, 20 and 30 psi in the device's chamber and determined the pressure drop, oil flow and oil temperature three times for each pressure. Since the capillary's length (0.411 m), the oil's viscosity (obtained by interpolation from the viscosity data in Table 3 – between 25 and 30 °C) and its flow were all known, we obtained the equivalent diameter through Equation 3, where ΔP is the pressure drop, μ is the viscosity, L is the capillary length, Q is the volumetric flow and D is the diameter.

$$\Delta P = \frac{64\mu LQ}{\pi D^4} \quad (3)$$

Table 4 shows the results obtained in calibrating the equipment; including the Reynolds number values at which the tests were conducted, attesting to the laminar regime ($Re < 3000$). We also listed the length/diameter ratio obtained for the capillary in each of the experiments. This is an important datum since the L/D should be greater than 115 to avoid the ''effect of the extremities''. From these results, we took the diameter of the capillary as equal to the average of the values obtained in each experiment, which implies a capillary diameter equal to 1.03 mm.

Table 2.
Results of the size exclusion chromatography.

Sample	M_n (g/mol)	M_w (g/mol)	Polydispersion
PAAm 1	16.000	53.100	3.32
PAAm 2	15.600	48.400	3.10
PAAm 3	46.400	215.800	4.65
PAAm 4	229.700	659.700	2.87
PAAm 5	234.200	922.900	3.94

Table 3.
Properties of the mineral oil - OP-10 (IPT 78).

Temperature (°C)	Viscosity (mPa · s)	Density (g/cm³)
20.0	14.13	0.8248
25.0	**11.74**	**0.8215**
30.0	**9.868**	**0.8182**
37.8	7.697	0.8131
40.0	7.208	0.8116
50.0	5.455	0.8050

Table 4.
Calibration of the capillary viscosimeter.

Chamber pressure	ΔP	Q	D	Re	L/D	T
(psi)	(Pa)	(m^3/s)	(mm)			(°C)
10	68948	4.30×10^{-7}	1.03	40	398	27.2
	68948	4.50×10^{-7}	1.04	41	393	27.2
	68948	4.64×10^{-7}	1.05	44	393	27.8
20	137895	8.80×10^{-7}	1.03	84	398	27.8
	137895	8.79×10^{-7}	1.03	84	398	27.8
	137895	8.88×10^{-7}	1.03	84	397	27.8
30	206843	1.31×10^{-6}	1.03	125	399	27.8
	206843	1.32×10^{-6}	1.03	126	398	27.8
	206843	1.30×10^{-6}	1.03	124	400	27.8

Pressure Drop Tests

We performed the pressure drop tests twice, and in all cases obtained concordant results. Figure 2 presents the results obtained in the pressure drop tests for various aqueous solutions of polyacrylamide. It can be seen that, as expected, the pressure drop diminishes as the polymer's molar mass increases, when compared with the pressure drop for pure distilled water.

Table 5 summarizes the drag reduction (DR) results obtained for all the fluids (the pressure drop values were taken at a Reynolds number equal to 7000).

Samples PAAm 1 and PAAm 2 did not present the expected coherence, probably because the molar mass numbers are very near each other and relatively very low. This can be demonstrated by observing the drag reduction percentage for PAAm 3, which has a molar mass well above those of samples PAAm 1 and PAAm 2: the drag reduction percentage of its solution is only slightly greater than for the other two solutions. In the region of the greatest molar mass (PAAm 4 and PAAm 5) there is an abrupt increase in the polymer's efficiency, evidencing the influence of higher molar mass on improved performance. In this study we did not achieve significant drag reduction percentages (above 70%) because the molar masses of

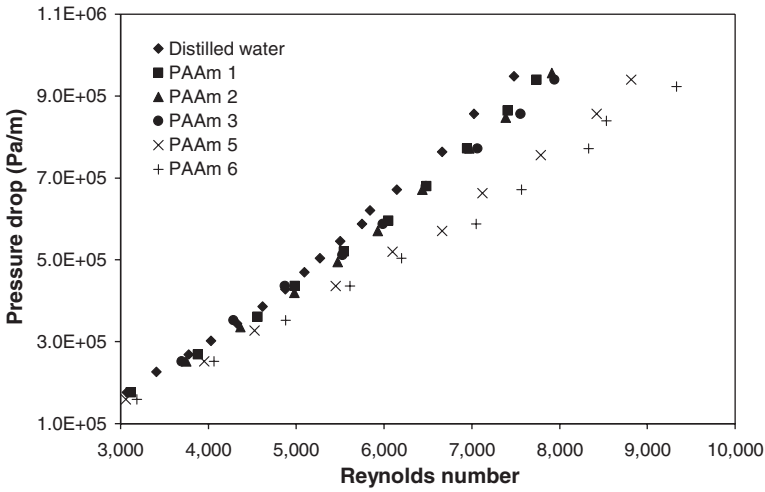

Figure 2.
Pressure drop for polyacrylamide solutions at 0.1 g/L.

Table 5.
Percentage of drag reduction (DR) for the polymer solutions at $Re = 7000$.

Solution	M_w (g/mol)	Pressure drop (Pa/m)	DR (%)
Distilled water	–	8.51×10^5	–
PAAm 1	53.100	7.86×10^5	7.6
PAAm 2	48.400	7.77×10^5	8.6
PAAm 3	215.800	7.70×10^5	9.5
PAAm 4	659.700	6.41×10^5	24.7
PAAm 5	922.900	5.98×10^5	29.7

the materials were far below those normally reported in the literature[33] for drag reduction systems.

Conclusions

As expected, the polymer's efficiency as a drag reducer was observed to grow with increasing molar mass. This is in line with what is known from the literature and attests to the validity of the methodology employed here: the device and method adapted to bench scale are reliable and adequate to conduct pressure drop tests and study the drag reduction properties of polymeric materials.

Acknowledgements: The authors thank CENPES/PETROBRAS, CNPq, ANP/FINEP and FAPERJ.

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