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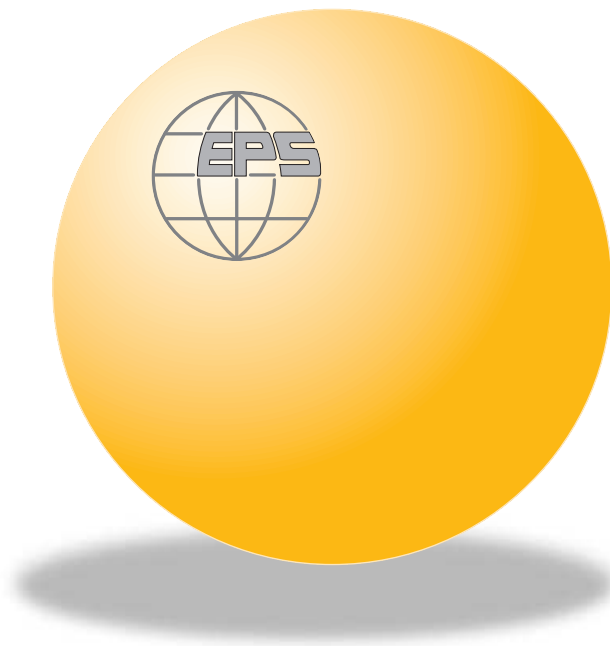
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Relation with the elongational viscosity**

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## Turbulent-drag reduction of polyelectrolyte solutions: Relation with the elongational viscosity

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**Abstract.** – We report measurements of turbulent-drag reduction of two different polyelectrolyte solutions: DNA and hydrolyzed polyacrylamide. Changing the salt concentration in the solutions allows us to change the flexibility of the polymer chains. For both polymers the amount of drag reduction was found to increase with the flexibility. Rheological studies reveal that the elongational viscosity of the solutions increases simultaneously. Hence we conclude that the elongational viscosity is the pertinent macroscopic quantity to describe the ability of a polymer to cause turbulent-drag reduction.

The phenomenon of turbulent-drag reduction describes the diminution of the dissipation in turbulent flow by adding tiny amounts of polymers. In this way for instance the amount of liquid that is transported in a pipe for a given pressure drop can be increased significantly. This implies a wide range of industrial applications, and consequently the effect, discovered in 1949 by Toms [1], has been studied intensively over the past decades (see, *e.g.*, [2–5]). In spite of this effort, the underlying physical mechanisms are ill understood and none of the existing theories matches the existing experimental data [6–8]. The key macroscopic property of these solutions that is known to be significantly different from that of the solvent is its elongational viscosity. Therefore, drag reduction is usually attributed to the elongational viscosity; however the precise connection remains unclear.

The elongational viscosity describes the resistance of a liquid to an elongational flow. In Newtonian liquids the elongational viscosity is just given by the shear viscosity times a factor of three, the Trouton ratio [9]. The addition of a small amount of polymers to the solvent does not change the shear viscosity significantly, however the elongational viscosity can increase by several orders of magnitude. Taking an elevated elongational viscosity into account, a

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qualitative explanation of drag reduction has been given by Landahl [10]: He suggests the elongational viscosity can suppress the occurrence of streaks —regions of flow with a high elongation rate— in the turbulent boundary layer. These boundary-layer instabilities lead to “blobs” of fluid that are ejected from the boundary layer into the bulk of the liquid and which generate the turbulence. An observation that provides support for the idea that the boundary layer is important was made by Cadot *et al.* [11]. They showed experimentally that drag reduction occurs only in boundary-layer-driven turbulence: if no boundary layers are present, indeed no drag reduction is observed upon addition of polymers. This implies that it is the way the turbulence is generated by the boundary layers that is altered by the addition of polymers.

To our knowledge, however, an explicit experimental proof of the relation between the elongational viscosity of a given polymer solution and its ability to cause turbulent-drag reduction is still missing mainly because the determination of the elongational viscosity of drag-reducing polymer solutions has proven difficult. It is the aim of this publication to provide this relation. In order to do so, we study both the elongational viscosity and turbulent-drag reduction of polymers that allow us to tune their chain flexibility. The large elongational viscosity of dilute polymer solutions is usually attributed to the resistance to stretching of the polymer chains in the elongational flow field. Therefore, flexible polymers should have a higher elongational viscosity. If in addition the phenomenon of drag reduction is indeed related to the elevated elongational viscosity, drag reduction should also increase with increasing chain flexibility. We show here that this is indeed the case using polyelectrolytes, for which the chain flexibility can be tuned by the addition of salt to the solvent. Adding salt leads to a screening of the electrostatic interactions between different parts of the same polymer, and can in this way lead to the winding of the polymer chains. At very low and very high salt, non-linear charging effects can become important; however, for the intermediate salt concentrations we use here, the chain is known to become more flexible upon increasing the ionic strength [12]. In that way the chain flexibility is altered *without* changing either the polymer chemistry or the chain length (the effects of which on drag reduction are still ill understood). For instance, Bauman *et al.* have measured the persistence length of DNA and find it to be a continuously decreasing function of NaCl concentration [13].

The first polyelectrolyte solution we use is therefore an aqueous solution of double-stranded  $\lambda$  DNA (48.5 bp) at the overlap concentration  $c^*$  of 40  $\mu\text{g}/\text{ml}$ . DNA is a model monodisperse polymer and its physical properties, for instance the relaxation time, are very well defined [14]. Our solutions contained a 10 mM Tris and 1 mM EDTA buffer (alternatively we also use a 2 mM Tris buffer) and the NaCl concentration was varied from 0 to 10 mM, changing the persistence length by a factor of three and the relaxation time from about 10 to 30 ms. The second polyelectrolyte used was 40  $\mu\text{g}/\text{ml}$  hydrolyzed polyacrylamide (HPAA) with a molecular weight of  $7 \times 10^6$  amu in water with NaCl concentrations varying from 1 mM to 18 mM.

First the shear-rate-dependent viscosity  $\eta(\dot{\gamma})$  of our samples was measured by use of a standard rheometer (Reologica Stress Tech) with a cone plate geometry that assures a laminar flow (fig. 1). In the range  $100 \text{ s}^{-1} < \dot{\gamma} < 2000 \text{ s}^{-1}$  all HPAA samples show shear thinning, the effect becoming less pronounced at higher salt concentrations. This was to be expected, as stiffer polymers (*i.e.*, polymers with a larger persistence length) show in general stronger shear thinning and a higher zero-shear viscosity, as also observed in our rheological measurements. Normal stress measurements show that the first normal stress coefficient does not depend strongly on the salinity; the relaxation time of the polymers thus decreases with increasing salt, mainly because of the decreasing viscosity. The DNA solutions showed only a slight shear thinning and no dependence on the salt concentration could be detected. This is because their viscosity is dominated by the solvent viscosity. At a shear rate of  $\dot{\gamma} = 2000 \text{ s}^{-1}$ , comparable

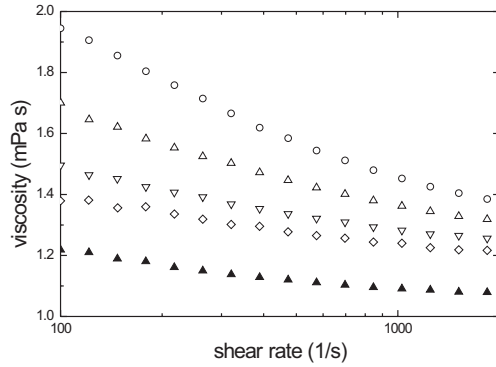


Fig. 1

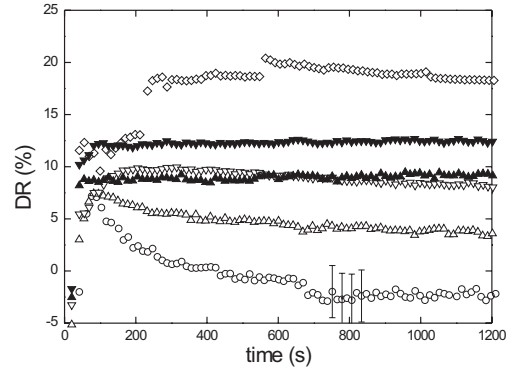


Fig. 2

Fig. 1 – The shear-dependent viscosity of the different polymer solutions. Open symbols: aqueous HPAA solutions 1 mM NaCl (circles), 2 mM (up triangles), 7 mM (down triangles), 18 mM (diamonds). Filled symbols: aqueous DNA solution 0 mM NaCl (up triangles).

Fig. 2 – The turbulent-drag reduction DR as a function of time at a constant stress of 8 Pa yielding a Reynolds number  $Re \approx 2000$ . Filled symbols: DNA solutions 10 mM NaCl (down triangles), the other symbols as in fig. 1. The error bars indicate the statistics of three consecutive measurements.

with the highest shear rates used in the drag reduction experiments, the shear viscosities for the aqueous HPAA solutions varies in between  $1.22 \text{ mPas} < \eta < 1.38 \text{ mPas}$  with the salt concentration and for the aqueous DNA solutions the viscosity is  $\eta \sim 1.08 \text{ mPas}$ . Our rheological measurements did not reveal any measurable normal stresses within the resolution of  $N_1 \approx 1 \text{ Pa}$  of the rheometer for the aqueous  $40 \mu\text{g/ml}$  solutions employed here.

To investigate turbulent-drag reduction we measured the drag of a turbulent flow of the different liquids in a Couette cell with a gap  $\delta = 1 \text{ mm}$ . Even if the industrial implications of turbulent-drag reduction are more likely to be pipe flow; this is in fact a rather common way to characterize polymer solutions for their ability to exhibit drag reduction [15,16]. A further advantage of this setup with a high surface-to-volume ratio is to probe directly boundary-layer effects.

Drag reduction measurements were performed on our standard rheometer. It was driven in controlled-stress mode, and drag reduction DR is defined as the normalized difference of the drag  $d$  on the inner cylinder by pure water and by the polymer solution, respectively, at same Reynolds number  $DR = (d_{\text{H}_2\text{O}} - d_{\text{pol}}) / d_{\text{H}_2\text{O}} \times 100\%$ . The Reynolds number is defined as  $Re = \frac{\Omega r \delta \rho}{\eta}$ ,  $\Omega$  being the rotation speed of the inner cylinder,  $\rho$  the liquid density and  $\eta$  the solvent viscosity.

Figure 2 shows the measured drag reduction as a function of time for a Reynolds number  $Re \approx 2000$ . Both for the DNA and for the HPAA solution DR is found to depend on the salt concentration in the solvent: drag reduction increases with increasing salt. For the DNA solution the results are qualitatively as for the HPAA, but the effects are less pronounced.

We believe the interesting temporal behavior for times  $t \lesssim 400 \text{ s}$  to be a rather complicated mixture of disentanglement of different polymer chains [11], rupture of the individual polymer chains by the strong flow [3], and relaxation of the flow towards a steady state. In addition to the data shown here, at longer times we observe a tendency to smaller values of drag reduction, probably due to further degradation of the polymers [15,16].

Drag reduction as a function of the Reynolds number is shown in fig. 3. For each new

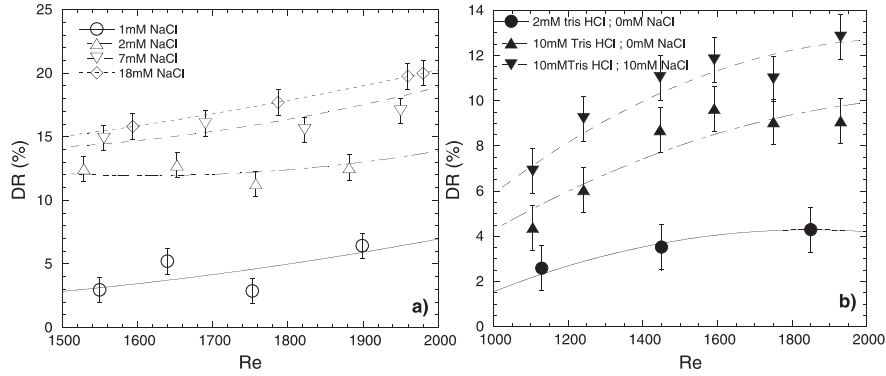


Fig. 3 – The turbulent-drag reduction DR as a function of the Reynolds number  $Re$  for 40  $\mu\text{g/ml}$  HPAA (a) and 40  $\mu\text{g/ml}$  DNA (b) solution.

Reynolds number the system was given 60 seconds to reach a steady state, a reasonable compromise in view of the different temporal effects discussed above. For all the solutions, we observe an increase of Drag reduction with increasing ionic strength. We checked that this is not due to our use of the Couette cell, or the very moderate Reynolds numbers employed here by repeating the experiments in the turbulence cell of Cadot *et al.* [11]. These high-Reynolds-number experiments gave very similar results: the highest Drag reduction measured with HPAA for a  $Re \approx 4.10^5$  was  $DR \sim 30\%$ , rather close to the drag reduction  $DR \sim 20\%$  measured with the Couette cell. The complete study of drag reduction at high Reynolds number will be published elsewhere [17].

Having measured the effect of salt on drag reduction<sup>(1)</sup>, we now turn to the elongational viscosity. As the velocity fluctuations in turbulence are violent, and rapidly change direction, it is unlikely that the polymer extension in such flows reaches a steady state. The pertinent experiment is therefore to study incipient (startup) elongational flow, and measure the response of the polymer solutions to that.

In order to measure the dynamic elongational viscosity  $\eta_e(t)$  of our solutions, we followed the method proposed by Bazilevskii *et al.* [19] and further developed by Amarouchene *et al.* [20]. Therein the authors describe the detachment process of a droplet of a diluted polymer solution from a capillary. The addition of a small amounts of flexible polymers to water inhibits the finite-time singularity break-up [21] of the droplet, and a cylindrical filament is formed between the capillary and the droplet. The flow profile in the filament is purely elongational and by balancing the capillary forces to the elastic stresses, the elongational viscosity  $\eta_e(t)$  can be extracted from the measured filament diameter  $h(t)$ . The elongational viscosity  $\eta_e(t)$  is time dependent because in the course of the experiment the polymers are more and more stretched by the flow. The experiments reveal that the temporal behavior of  $h(t)$  is exponential, implying a unique thinning regime for which the elongational rate  $\dot{\epsilon} = -2\frac{\partial_t h}{h}$  remains constant.

Recently, Anna and Mc Kinley [22] have shown that filament thinning techniques analogous to the one used here lead to measures of the elongational viscosity that are consistent with the more established filament stretching techniques. The latter cannot be employed here since they only allow for measurements for much more viscous solvents (typically 1 Pas) [22].

It turns out that for the aqueous solutions used in the DR experiments, the droplet de-

<sup>(1)</sup>In a recent paper, Choi *et al.* [18] have reported on the drag reduction properties of DNA at lower concentrations but higher Reynolds numbers. However, their focus was on studying the degradation introduced by the high stretching fields and no correlation with the elongational viscosity was given.

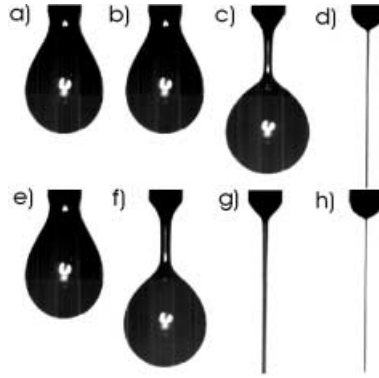


Fig. 4 – The detachment process of the droplet for the 40  $\mu\text{g}/\text{ml}$  DNA solutions with 80/20 vol% glycerol-water as solvent and a), b), c), d) 0 mM NaCl and e), f), g), h) 10 mM NaCl. The rows show different time steps  $t$  in regard to the moment  $t_c$  when the filament breaks. a), e):  $t_c = 120$  ms; b), f):  $t_c = 94$  ms; c), g):  $t_c = 53$  ms; d), h):  $t_c = 20$  ms. The viscosity of the solvent is 80 mPas and the capillary used to study the droplet formation has a diameter of 1.2 mm.

tachment process is too fast to observe, even using a rapid camera (Photonetics) working at a 1000 frames/s. Increasing the solvent viscosity slows down the dynamics of the filaments sufficiently so that these can be followed, and the elongational viscosity can be determined. We will show below that these measurements suffice also to deduce the elongational viscosity of the aqueous solutions used in the drag reduction experiments.

The solvent viscosity could be adjusted by adding a certain amount of glycerol. Figure 4 shows the photographs of the detachment process for the DNA solution for the 0 mM and the 10 mM salt concentration. The trend can be observed directly on the pictures: the more flexible polymer has a higher elongational viscosity; it is evident from the figure that the filament thinning is much slower.

In the filaments, for the DNA solutions, the elongational rate varies with NaCl:  $\dot{\epsilon} = 90 \text{ s}^{-1}$  for low concentration and  $\dot{\epsilon} = 50 \text{ s}^{-1}$  for high concentration. In order to be able to compare different experiments, it is thus useful to introduce the so-called Hencky strain, the product of the elongation rate and the elapsed time  $\dot{\epsilon}t$ , which measures the total deformation of the fluid element containing the polymer. We define the zero of the Hencky strain for the moment when the filament is formed, *i.e.* when the flow is strong enough to interact with the polymers [20].

Figure 5 shows the elongational viscosities of the different samples, for different salinities as a function of the Hencky strain. Again both for the DNA and the HPAA,  $\eta_e$  depends strongly on the salt. For HPAA,  $\eta_e$  changes more than a factor of three between the lowest and the highest salinity, while there is still a factor of almost two observed for the DNA solution.

A prediction of all polymer flow models is that the elongational viscosity scales linearly with the solvent viscosity [23]. If this is true, we can directly extract the elongational viscosity of the aqueous solutions used in the drag reduction experiments from the elongational viscosities of the glycerol-water solutions. To verify this, we prepared a series of additional samples of 300  $\mu\text{g}/\text{ml}$  PAA in different glycerol-water mixtures. We use a rather high concentration (although we are still below  $c^* \sim 500 \mu\text{g}/\text{ml}$ ) because otherwise the rapid camera is too slow to quantitatively evaluate  $\eta_e$ . The addition of glycerol allows us to change the solvent viscosity  $\eta$  in the range  $10 \text{ mPas} \leq 80 \text{ mPas}$ . The inset of fig. 5 shows the Trouton ratio  $\text{Tr}$ , the measured elongational viscosity  $\eta_e$  of the polymer solutions divided by three times the viscosity of the solvent ( $\text{Tr}/3 \equiv 1$  for Newtonian liquids). The Trouton ratio of the different solutions perfectly

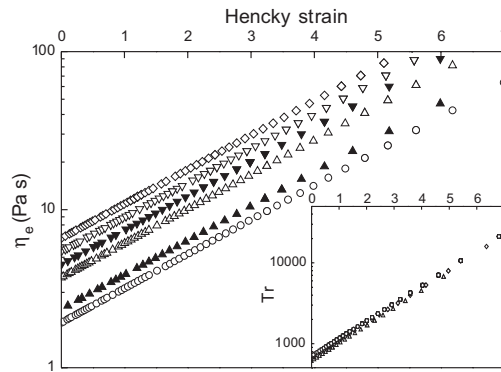


Fig. 5 – The elongational viscosity  $\eta_e$  for the different polymer solutions. The symbols are as in fig. 1, only the solvent is a 80/20 vol% glycerol-water mixture. Inset: the Trouton ratio  $Tr$  for solutions with  $300 \mu\text{g/ml}$  PAA in different water-glycerol mixtures and 0 mM salt. The solvent viscosities are  $\eta = 80$  (circles), 43 (squares), 20 (up triangles), 10 (diamonds) mPas.

collapses onto a single master curve. For even smaller viscosities, slight discrepancies can be observed, but here the dynamics becomes again too fast to allow for a precise determination of  $\eta_e$ . The perfect collapse also indicates that the chain flexibility is not modified by the addition of different amounts of glycerol. Therefore we can obtain the elongational viscosities  $\eta_e$  of the aqueous polymer solutions by dividing the data from the glycerol water solutions by the ratio of the solvent shear viscosities.

It is therefore now possible to relate the drag reduction directly to the elongational viscosity. The result is shown in fig. 6. We plot the drag reduction for a given Reynolds number as a function of the elongational viscosity  $\eta_e$  at a Hencky strain of 1. Drag reduction is shown to increase monotonically with the elongational viscosity for a given polymer and the data for the different polymers collapse, demonstrating that indeed the elongational viscosity is the pertinent macroscopic quantity to account for DR. As far as we can tell, this is the first explicit

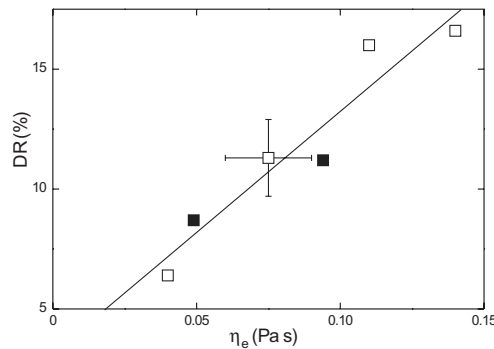


Fig. 6 – The drag reduction DR at a Reynolds number  $Re_{\text{poly}} = 1400$  as a function of the elongational viscosities of the aqueous polymer solutions, for different salinities at a Hencky strain of  $\dot{\epsilon}t = 1$ . To allow for a comparison between samples with a different shear viscosities, the Reynolds number  $Re_{\text{poly}}$  is calculated using the laminar shear viscosities of the polymer solutions at a shear rate  $\dot{\gamma} = 2000$ . Filled squares: DNA solutions, open squares: HPAAsolutions (the drawn line is a guide to the eye).

demonstration that the turbulent-drag reduction is directly connected with the elongational viscosity of a polymer solution.

These results, especially those on DNA, open the way to a microscopic understanding of both the enormous elongational viscosity dilute polymer solutions can have, and the surprising results thereof: turbulent-drag reduction. It has recently become possible to observe the deformation of the polymer chains due to flow of single DNA molecules using fluorescence microscopy [14]. Performing such an experiment on the filaments would allow to relate the extension of the individual polymer chains to the macroscopic stresses the chain extensions generate. If subsequently the polymer conformation is visualized in a turbulent boundary layer, an estimate of the extra stresses in the boundary layer could be obtained, which could be the key to the understanding of this phenomenon. These experiments are in progress.

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