

Drag reduction and solvation in polymer solutions

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SUMMARY: A model is described which explains drag reduction (DR) in dilute polymer solutions in terms of solvation of macromolecular chains and formation of relatively stable domains. The domains partly suppress the vortex formation, act as energy sinks, and also play a role in mechanical degradation in flow (MDF). We report ultrasonically determined solvation numbers for a series of copolymers with the same chemical structure but differing widely in their intrinsic viscosities. The solvation numbers confirm the model. Thus, we have a criterion for selection of DR agents with low MDF for: oil well operations; crude oil transport; fire fighting; high sewer throughput; irrigation; hydrotransport of solids; marine applications; and biomedical applications including the arteriosclerosis prevention.

Drag reduction (DR) in dilute polymer solution flow is a phenomenon very useful in a variety of applications^{1,2}: oil well operations, crude oil transport, fire fighting, increasing sewer throughput, irrigation, hydrotransport of solids in water and heating circuits, in hydraulic machinery and jet cutting, in marine applications and also in biomedical applications (arteriosclerosis prevention, since the phenomenon occurs constantly in blood flow^{3,4}). Moreover, the drag reduction capability has been associated with antimisting, important for mist-forming combustible liquids, for instance during filling airplane fuel tanks. Given the utility of DR, there is a number of explanations why it takes place, none of them generally accepted. One of us developed a model of the DR mechanism already in 1983⁵, but it remained a conjecture for lack of proof. Below we report direct experimental evidence now obtained which shows the validity of the model, plus point out results of computer simulations and other evidence supporting the model.

It is convenient to distinguish between the phenomenon itself (DR), and its quantitative measure λ defined as

$$\lambda = 1 - f/f_1 \quad (1)$$

often expressed in %; here f is the friction factor (drag coefficient, friction coefficient) for solution and f_1 the respective factor for the pure solvent. DR is known to occur not only in “simple” pipes or capillaries, but also in beds filled for instance with glass wool and/or nickel powder. The problem is hardly of academic interest only. It has been known for decades that DR is accompanied by mechanical degradation in turbulent flow (MDF)⁶. Understanding DR should help in the development of DR agents with slow MDF.

Before defining the model we note two pertinent facts. First, as demonstrated in particular by Forsman⁷, there

exists an intimate connection between conformational statistics and chain dynamics. DR takes place in highly dilute polymer solutions, and even there the existence of the connection is clearly visible in Brownian dynamics computer simulations, both static⁸ and in flow⁹. Second, the importance of polymer + solvent interactions is demonstrated by ultrasonic absorption and shear viscosity studies of solutions of a number of homo- and copolymers by Alig, Wartewig and coworkers^{10,11}. The role of the solvent shows up clearly also in the already classical work of Zakin, Hunston and coworkers (ZH) on DR^{12–14}. ZH demonstrated that the polymer concentrations c necessary for equal drag reduction λ are several times greater in poor solvents as compared to a good solvent. They have also found that under given flow conditions there is much more MDF in poor solvents than in good solvents. One can use the well-known Flory-Huggins-Staverman interaction parameter χ as a measure of the quality of the solvent; negative or low positive values of χ correspond to good solvents.

It is clear from the above that any model of DR has to take into account both macromolecular conformations and the polymer + solvent [1 + 2] interactions. The model of DR originally proposed in ref.⁵ will now be briefly described – reworded in terms of the solvation number s_{1+2} (measurements of which are reported below); s_{1+2} is the number of solvent molecules attached to a repeat unit of the polymer. In the static situation the values of s_{1+2} along the chain do not vary in a significant way. When flow takes place, however, particularly at values of the Reynolds number above the turbulence limit, some of the polymer chain sequences will become aligned with the flow. Given numerous direction reversals so intrinsic to macromolecular chains, however, there will be also other sequences approximately perpendicular to the flow. The

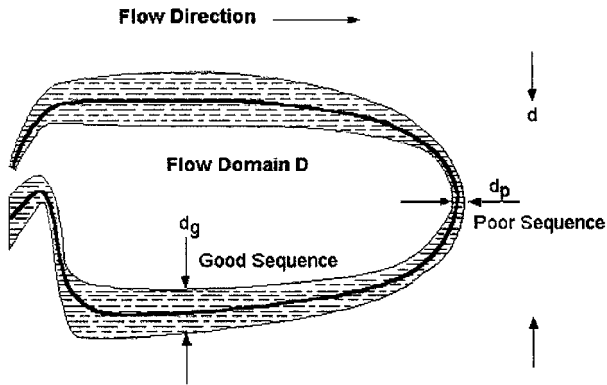


Fig. 1. Solvation and domain structure in flow of dilute polymer solutions. d is the approximate domain diameter; other explanations in text. The angle ψ between the flow direction and a given sequence is here $\approx 0^\circ$ for the good sequence indicated (and for the top one too) while it is $\approx 90^\circ$ for the poor sequence in the front of the domain

situation is depicted in Fig. 1 as a two-dimensional cross-section through the solution. Instead of dealing with all possible values of the angle ψ between the flow direction and a given sequence, we choose to represent the chain by sequences of two kinds, good with $\psi \approx 0^\circ$ and poor with $\psi \approx 90^\circ$. In obvious notation, the total number of sequences $b = b_g + b_p$. The degree of polymerization $r = br_b$, where r_b is the average number of repeat units in a sequence. If the chains are copolymeric, then exists an extra reason for the presence of sequences of at least two kinds.

Consider first a good sequence. The solvation number s_{g1+2} will not undergo large changes in flow as compared to the static situation. In other words, because of the alignment of the sequence with flow, most solvent molecules attached to the sequence at rest will now be moving in unison with the flow. Some sequences which are nearly but not quite aligned with the flow will become *more* aligned. Thus, the assumption of separation of the sequences into two classes will now approach closer the real situation. Then partial elongation of chains will take place^{15–17}. As demonstrated by Zisenis, Prötzel and Springer¹⁷, the elongation in the flow direction is accompanied by contraction in the perpendicular direction. Clearly creation of extended or stretched conformations favors the existence of good sequences. By contrast, a poor sequence will have $s_{p1+2} < s_{g1+2}$ since the turbulence will partly denude such sequences. This is shown in Fig. 1, with the diameters of the two kinds of sequences shown as $d_p < d_g$. Fig. 1 can represent the structure at rest as well as in laminar and turbulent flows, except for the fact that the ratio b_g/b for the chain will be different in each case. The most important feature shown in the figure is the formation of a *domain* – shown here also in its two-dimensional cross-section. Its thickness in the direction perpendicular to the plane is at least d_p . Moreover, below

and above the sequences displayed we might have similar good sequences approximately aligned along the flow, what provides a still larger domain size in the z direction. In solutions of various polymer concentration there have been observations of long-range heterogeneities (LRHs)^{18–20} – what agrees well with our domain model.

The popular definition of flow turbulence as “eddies within eddies within eddies” is actually quite convenient for our purposes. When the flow starts, the domains *partly suppress the vortex formation* – one key function of the DR macromolecules. Eddies are smaller than the domains, and the number of eddies per unit volume is much higher outside the domains than in the domain interiors. Our Brownian dynamics simulation of dilute solution flow show, first of all, the importance of polymer + solvent interactions⁹. A combinatorial formula for the number of chain overlaps which neglects such interactions²¹ gives too low numbers of interchain contacts, except at the lowest segment number densities. In the same simulations at high shear rates the average number of entanglements per chain and the average number of interchain contacts decrease along with an increase in the shear rate⁹. This should favor the formation of more domains and an increase in drag reduction – as indeed was observed experimentally by Kim and coworkers^{22,23}. Moreover, for eddies already in existence the domains *act as energy sinks* – the *second* role of domains in producing DR. The energy dissipation involves localized sequence motions and occasional partial denuding of a sequence under the action of the flow. However, a solvent molecule previously solvated – but now separated from the chain under the action of an eddie – will be replaced by another solvent molecule. Thus, the average solvation number consistent with the polymer + solvent pair and the Reynolds number will be preserved. This unless an MDF event (chain scission) occurs in the flow; this is the *third* mechanism of energy dissipation, one however that causes a decrease of λ as a function of time.

DR is known to occur at polymer concentrations of a few ppm (1). Oliver and Bakhtyarov²⁴ report DR in aqueous high molecular mass poly(acrylamide) solutions even at $c = 0.02$ ppm. The low-ppm DR results also support the model proposed in ref.⁵: the very presence of macromolecular chains causes solvation and creates domains powerful enough to produce such significant effects.

For a given solvent + polymer (1 + 2) pair, the solvation number can be calculated from the Passynski equation^{25,26}:

$$s_{1+2} = (1 - \kappa_s/\kappa_{s1})(M_u/M_1)[(100 - x)/x] \quad (2)$$

the adiabatic (also called isoentropic) compressibility $\kappa_s = V^{-1}(\partial V/\partial P)_S$, where V is the volume, P pressure and S entropy; M_u is the molecular weight of the repeat unit of the polymer, so that in a copolymer a weighted average

Tab. 1. Experimental results for a number of graft copolymers

Symbol	Amount of AA in mol	Amount of Ce ⁺⁴ in mmol	Intrinsic viscosity $[\eta]/(\text{ml} \cdot \text{g}^{-1})$	Solvation number s_{1+2}	100 ppm	Drag reduction λ in %		
						300 ppm	800 ppm	1000 ppm
Ia	0.140	0.0625	470	15	44.3	59.1	63.6	64.8
III d	0.210	0.250	350	15	31.8	52.3	59.1	61.4
Ib	0.140	0.125	400	13	35.4	56.1	61.0	62.2
IIb	0.070	0.125	300	12	27.9	47.7	58.1	60.5
Ic	0.140	0.250	310	11	20.2	40.5	53.6	56.0
II d	0.210	0.375	330	10	12.2	22.2	36.7	37.8
III b	0.070	0.250	140	10	5.4	15.9	19.6	20.7
II a	0.035	0.0625	115	9	8.1	16.3	27.9	31.4
I d	0.140	0.375	220	8	5.8	9.3	18.6	20.9
I e	0.140	0.438	100	8	4.65	8.1	16.3	17.4

In all cases the amount of PVA was 0.008 mmol. The λ thevalues all pertain to aqueous solutions.

over the types of units present is required; the index 1 pertains to pure solvent as before, the quantities without an index to solutions, except that x is the weight of polymer in 100 g of the solution. We have determined experimentally the ultrasonic velocity c and the mass density ρ and computed the compressibility using the standard formula $\kappa_s = c^{-2}\rho^{-1}$. To check the validity of Eq. (2), we have studied two aqueous drag reducers of the same chemical nature [poly(ethylene oxide)] but with different degrees of polymerization r (Polyox coagulant and Polyox WSR N-750, both from BDH, United Kingdom, the first with molecular weight $M = M_{ur} = 5.0 \cdot 10^6$, the second with $M = 3.0 \cdot 10^5$). For each polymer, experiments were performed for different polymer concentrations c and the resulting s_{1+2} values extrapolated to infinite dilution. In each case the result was $s_{1+2}(c \rightarrow 0) = 3$. The fact that $s_{1+2}(c \rightarrow 0)$ is independent of r , with r varied over a whole order of magnitude, confirms the physical significance of s_{1+2} as defined by Eq. (2).

In Tab. 1 we list experimental results for a number of graft copolymers. The model proposed in ref.⁵⁾ and characterized above suggests that grafting can create additional domains. We did not wish to introduce extra factors, such as differences in chemical structures, which could obscure the situation. Poly(vinyl alcohol) (PVA) backbones were grafted with varying amounts of acrylamide (AA) in the presence of also varying amounts of ceric ammonium nitrate (which as a catalyst affects strongly M values as well as the intrinsic viscosity $[\eta]$); experimental details will be provided elsewhere. The λ values listed pertain to the initial drag reduction; values of λ as a function of the number of passes are available also and will be reported later. The number of passes is here the number of measurements performed on the same solution so as to investigate changes in λ caused by MDF.

Perusal of the results in Tab. 1 confirms the key assumption of the model developed in ref.⁵⁾: *the DR efficacy λ goes symbotically with the extent of solvation of*

the polymer, the latter now represented by s_{1+2} . Some minor deviations in the table appear within limits of the experimental accuracy; while λ values for III b are “out of order”, the s_{1+2} value for that polymer is larger only by a single unit than s_{1+2} of II a which is next in the table. Thus, the key assumption of the model proposed in 1983⁵⁾ is now confirmed.

Not only the model, the present experimental results, the computer simulations⁹⁾ and the experiments of Kim et al.^{22,23)} produce a single picture. A number of other findings also fall into place. Decades ago Debye²⁷⁾ has proven theoretically that a freely jointed polymer chain would rotate as a whole, instead of aligning with the flow and elongating. Since alignment and elongation are found repeatedly, clearly polymer chains in dilute solutions are not fully flexible – contrary to the freely jointed chain model. Our solvation theory explains this lack of flexibility. Even if we confine ourselves to the situation at rest, Flory²⁸⁾ has obtained values of configurational dimensions of polymers often twice those calculated assuming free rotation about all single bonds – what our model explains at the same time. Kulicke and collaborators¹⁾ report that a single chain can cause DR; the domain formation in our model explains their finding. The 0.02 ppm DR reported by Oliver and Bakhtiyarov²⁴⁾ and already mentioned is explained as well. As noted above, the very presence of macromolecular chains creates structures stable enough to cause DR. Moreover, Donohue, Tiederman and Reischman²⁹⁾ found that low speed streaks originating from a conduit wall lift off, but after neither oscillating nor bursting return to the wall. Our domains such as that shown in Fig. 1 will reflect such streaks. Still further, Hunston and Reischman³⁰⁾ have shown that only chains above a certain length participate in DR; clearly too short chains cannot form domains. Our model has led to a relation between λ and time t (the MDF effect) which has been confirmed experimentally for several polymer + liquid pairs³¹⁾. The findings of Zakin, Hunston and cowor-

kers concerning the effects of solvent quality on λ and on MDF^{12-14} not only fit with our model; an attempt to explain their results was in fact the beginning of the formulation of the model.

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