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UMI
STUDY OF THE INTERACTIONS BETWEEN POLY(ETHYLENE OXIDE) AND ANIONIC SURFACTANTS IN ELONGATIONAL FLOW

by

Luis Manuel Smitter

A Dissertation Submitted to the Faculty of the
DEPARTMENT OF CHEMICAL AND ENVIRONMENTAL ENGINEERING
In Partial Fulfillment of the Requirements
For the Degree of
DOCTOR OF PHILOSOPHY
WITH A MAJOR IN CHEMICAL ENGINEERING
In the Graduate College
THE UNIVERSITY OF ARIZONA

2001
As members of the Final Examination Committee, we certify that we have read the dissertation prepared by Luis Manuel Smitter entitled "Study of the Interactions Between Poly (Ethylene Oxide) and Anionic Surfactants in Elongational Flow" and recommend that it be accepted as fulfilling the dissertation requirement for the Degree of Doctor of Philosophy.

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Final approval and acceptance of this dissertation is contingent upon the candidate's submission of the final copy of the dissertation to the Graduate College.

I hereby certify that I have read this dissertation prepared under my direction and recommend that it be accepted as fulfilling the dissertation requirement.

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STATEMENT BY AUTHOR

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<th>Definition</th>
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<td>$b_i$</td>
<td>Brownian motion force of bead ‘i’</td>
</tr>
<tr>
<td>$b_k$</td>
<td>Length of segment associated with the freely jointed chain</td>
</tr>
<tr>
<td>$c^*$</td>
<td>Coil overlap concentration</td>
</tr>
<tr>
<td>$c^-$</td>
<td>Limiting polymer concentration for transient network formation in extensional flow</td>
</tr>
<tr>
<td>$C_p$</td>
<td>Polymer concentration</td>
</tr>
<tr>
<td>$D$</td>
<td>Diameter of the capillaries that constitute the opposed-jets</td>
</tr>
<tr>
<td>$D$</td>
<td>Rotatory diffusivity of the dumbbell</td>
</tr>
<tr>
<td>$De_{ext}$</td>
<td>Deborah number in uniaxial extensional flow</td>
</tr>
<tr>
<td>$De^{c-s}_{ext}$</td>
<td>Deborah number for coil-stretch transition in uniaxial extensional flow</td>
</tr>
<tr>
<td>$De^{s-c}_{ext}$</td>
<td>Deborah number for stretch-coil transition in uniaxial extensional flow</td>
</tr>
<tr>
<td>$De_{shear}$</td>
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</tr>
<tr>
<td>$E$</td>
<td>Rate of deformation tensor</td>
</tr>
<tr>
<td>$F^c$</td>
<td>Connector force law of the spring</td>
</tr>
<tr>
<td>$F_d$</td>
<td>Drag force</td>
</tr>
<tr>
<td>$H$</td>
<td>Constant given by $H = 2kT\beta^2$</td>
</tr>
<tr>
<td>$I$</td>
<td>Unit tensor</td>
</tr>
<tr>
<td>$k$</td>
<td>Boltzmann’s constant</td>
</tr>
<tr>
<td>$L$</td>
<td>Dimensionless fully extended length of the polymer molecule</td>
</tr>
<tr>
<td>$M_w$</td>
<td>Viscometric average molecular weight of the polymer</td>
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<tr>
<td>$n$</td>
<td>Normal vector to a surface</td>
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<tr>
<td>$n_c$</td>
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</tr>
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</tr>
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<tr>
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<tr>
<td>$\mathbf{R}$</td>
<td>End-to-end vector</td>
</tr>
<tr>
<td>$\dot{\mathbf{R}}$</td>
<td>Rate of growth of $\mathbf{R}$</td>
</tr>
<tr>
<td>$R_{eq}$</td>
<td>Equilibrium end-to-end distance</td>
</tr>
<tr>
<td>$R_g$</td>
<td>Radius of gyration</td>
</tr>
<tr>
<td>$R_{g,eq}$</td>
<td>Equilibrium radius of gyration</td>
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<tr>
<td>$R_{g,eq0}$</td>
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<tr>
<td>$R_0$</td>
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<tr>
<td>$\mathbf{R}^*$</td>
<td>Equilibrium end-to-end distance</td>
</tr>
<tr>
<td>$&lt;\mathbf{RR}&gt;$</td>
<td>Average value of $\mathbf{RR}$ over all possible polymer configurations</td>
</tr>
</tbody>
</table>
NOMENCLATURE – Continued

\(< R^2 >_0 \) Mean square end-to-end distance (same as \( R_{eq}^2 \))

\( r_0 \) Bead radius

\( S \) Dimensionless conformation tensor

\( T \) Temperature

\( t \) Time

\( t' \) Dimensionless time

\( t_{char} \) Characteristic time

\( t_p \) Polymer stress vector

\( u \) Relative velocity between the beads

\( v \) Fluid velocity

\( v_i \) Velocity of bead \( 'i' \)

\( v_f \) Fluid velocity at the bead location \( r=r_i \)

\( v_i \) Contribution from the other bead to the velocity of the solvent at bead \( 'i' \)

\( v_{p,0} \) Fluid velocity at the bead location in the absence of other beads

\( V_v^{max} \) Hydrodynamic volume of the polymer/surfactant complex at PSP

\( V_{hp} \) Hydrodynamic volume of the polymer

\(< RR > \) Upper-convected time derivative of \(< RR >\)

\( \beta^2 \) Constant given by Eq. 6-5

\( \delta \) Separation between the opposed-jets

\( \dot{\varepsilon} \) Strain rate

\( \dot{\varepsilon}_c \) Critical strain rate for coil-stretch transition

\( \dot{\varepsilon}_p \) Critical strain rate for stretch-pipe transition

\( \dot{\varepsilon}_n \) Critical strain rate for transient network formation

\( \gamma \) Shear rate

\( \eta \) Solution viscosity

\( \eta_I \) Excess viscosity due to the interactions between polymer and surfactant

\( \eta_{f, PSP} \) Excess viscosity due to the interactions between polymer and surfactant at the PSP

\( \eta_{max} \) Maximum viscosity of the solution

\( \eta_p \) Contribution of the polymer to the solution viscosity

\( \eta_s \) Contribution of the solvent to the solution viscosity

\( \eta_m \) Viscosity of a Newtonian fluid under uniaxial extension
NOMENCLATURE – Continued

\( \eta_{sp} \)  Specific viscosity
\( \eta_{\text{surf}} \)  Excess viscosity of the solution due to the presence of surfactant
\( \bar{\eta}_0 \)  Zero-shear rate solution viscosity
\([\eta]\)  Intrinsic viscosity
\( \lambda \)  Polymer relaxation time
\( \lambda_e \)  Polymer disentanglement time
\( \nu \)  Number concentration of polymer (number of polymer molecules per unit volume)
\( \tau_p \)  Corrected stress tensor due to the polymer
\( \tau'_p \)  Stress tensor due to the polymer
\( \tau_s \)  Stress tensor due to the solvent
\( \Delta P \)  Pressure drop
\( \psi_1 \)  First normal stress coefficient
\( \psi_2 \)  Second normal stress coefficient
\( \zeta \)  Friction coefficient
\( \zeta_0 \)  Friction coefficient when the molecule is at equilibrium
\( \Omega \)  Oseen tensor
\( \Psi(R) \)  Probability distribution of end-to-end vectors
\( \Psi_o(R) \)  Equilibrium probability distribution of end-to-end vectors
The rheology of polymer solutions is important in a wide variety of applications. In particular, solutions of high-molecular-weight, flexible polymers exhibit an increase in their apparent extensional viscosity with strain rate under extensional flow conditions. This extension thickening is due to formation of transient entanglements of polymer molecules. Certain commercial fluids contain both polymers and surfactants that might interact at the molecular level. These interactions affect the conformation of the polymer chain and, therefore, the rheological behavior of the solution. For instance, addition of anionic surfactants to solutions of nonionic polymers is known to induce increases in the shear viscosity of aqueous solution. This work investigates the behavior of aqueous solutions of a high-molecular-weight poly(ethylene oxide) (PEO), a nonionic, flexible polymer, and the anionic surfactants sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulfonate (SDBS) and a commercial α-olefin sulfonate (AOS) in extensional flows. The extensional rheology of polymer/surfactant solutions is studied in an opposed-jets device, which generates a flow field close to uniaxial extension. For PEO/SDS mixtures, the results show that formation of micellar aggregates of SDS along the PEO chains results in an increase in the strength of extension thickening of PEO solutions by promoting intermolecular interactions between polymer chains. The minimum PEO concentration required to form intermolecular entanglements is substantially reduced in the presence of micellar aggregates. In solutions containing NaCl, intramolecular interactions are observed at low PEO concentrations. These reduce the strength of
extension thickening. Addition of a co-solvent is investigated. The presence of alcohols in the aqueous solutions affects their rheology by changing the solvent nature for both PEO and SDS. In particular, n-octanol promotes aggregation of SDS along the PEO chains, enhancing intermolecular network formation in extensional flow. Results with mixtures of PEO with sulfonated surfactants (SDBS and AOS) show that both intermolecular and intramolecular interactions are promoted by these surfactants, depending on PEO concentration and molecular weight. The effect of ageing on these polymer/surfactant systems was studied. In extensional flows, extension thickening is suppressed in solutions of PEO with SDBS or AOS over a few-day period, whereas PEO and PEO/SDS solutions show no change.
CHAPTER I
INTRODUCTION

1.1. Polymer/Surfactant Solutions

Polymer solutions and surfactant solutions are of extreme importance in many applications in nature and technology. It is also well known that mixtures of these two solutes reveal unusual interaction effects. For instance, the ability of a surfactant to lower the interfacial tension between an aqueous solution and some other phase is modified by the presence of a polymer in solution (1). Figure 1.1 shows the effect of poly(ethylene oxide) (PEO) on the surface tension of aqueous solutions with the surfactant sodium dodecyl sulfate (SDS), for different surfactant concentrations (2). It is observed that for aqueous solutions of SDS, the surface tension decreases with SDS concentration. This is due to the adsorption of surfactant molecules at the air/water interface. As the SDS concentration increases, a plateau is reached, indicating the formation of micelles in the bulk solution from unassociated molecules of surfactant. The concentration at which this occurs is called the critical micelle concentration (CMC). In the presence of PEO, there is a change of slope in the surface tension curve at a certain concentration ($C_1$) lower than the critical micelle concentration. Then, the decrease in surface tension occurs more gradually, up to a concentration denoted by $C_2$, where the slope in the surface tension curve changes again, until at a concentration denoted by $C_3$, the surface tension reaches a constant value. The interpretation of these observations is as follows: at the concentration $C_1$, micelle-like structures (micellar aggregates) associate with the polymer forming polymer-surfactant complexes. The association continues until at a concentration between
C₂ and C₂', the polymer is saturated with aggregates. At a surfactant concentration above C₂, free micelles are present in solution. These interactions as well as the structure of the mentioned complexes will be discussed in more detail throughout this work.

![Graph showing surface tension as a function of SDS concentration.](image)

Figure 1.1. Surface Tension at 25°C of SDS in water (1) and of a 100 ppm PEO solution (2) as a function of SDS concentration. The average molecular weight of the PEO is 2x10⁶.

The interactions between surfactants and polymers in aqueous solution have been extensively studied during the last decades, and it is still a subject of interest. Solutions of mixtures of polymer and surfactant have properties that are important for a wide range of industrial applications, such as flotation processes, foaming controls, detergency, cosmetics, coatings, paints, foods, chemical treating systems, pharmaceutics, biological systems and enhanced oil recovery.

Different combinations of polymers and surfactants are known to induce substantial
increases in the viscosity of aqueous solutions, and at the same time the structures formed exhibit shear thinning characteristics, thus providing opportunities for rheology control, which is important in latex paints. Gel formation has also been observed, and interest in aqueous gel technology is traditional in the food and pharmaceutical industries, as well as in the cosmetics and detergents fields.

Surfactant solutions are known for their ability to dissolve organic, water-insoluble materials. Complex formation with a nonionic polymer decreases the critical aggregation concentration of the surfactant; therefore enhanced solubilization by the complex can be anticipated. This effect has been confirmed using water-insoluble dyes, hydrocarbons and nearly insoluble fluorescers. This property is also useful in terms of designing a process for clean-up of aqueous streams (3). Due to the polymer/surfactant association in solution, it is expected that they influence the solubility of each, as well as that of a third component. By means of solubilization processes, there is the possibility of regenerating the original polymer in a different state (fibers, films, etc.).

Another application (4) is the use of polymer/surfactant aqueous solutions as media for inorganic crystallization. The goals are not only to control the size, shape, morphology and polydispersity of the crystals, but also to produce novel organic/inorganic nanocomposite materials with specific properties. Leontidis et al. (4) studied the formation of lead sulfide (PbS) crystallites in the vicinity of micelles of SDS bound to PEO chains on addition of lead and sulfide to the polymer-surfactant solution. The production of nanocrystalline PbS was studied recently, since PbS is a prominent semiconductor.
Surfactants in solution are known to induce swelling of the outer layer of the human skin, where anionic surfactants have been reported to produce the highest levels of swelling. Evidence suggests that lowering the monomer concentration of the surfactant corresponds to a lowering of irritation, and such a reduction can be achieved in the presence of a polymer (5). At the same time, results show that a cationic cellulose derivative (a polymer) significantly reduces irritation caused by sodium dodecyl sulfate, shampoos and soap. Additional evidence with polyvinyl pyrrolidone shows similar tendencies (6).

Another interesting application of polymer and surfactant interactions is related to control of drug delivery. It has been determined that addition of anionic surfactants in a drug tablet containing hydroxypropylmethylcellulose (HPMC) as binder results in a prolonged time of drug release in an aqueous medium (7). There is a considerable interest in the use of gels as the delivery medium, and to date the classical gelling polymers have been the main types employed to provide the delayed diffusion characteristics associated with these media (3).

Appropriate choice of polymers and surfactants allows for modification of surface characteristics of chosen solids, since both can adsorb in such surfaces. This is the case of conditioning of hair and skin (3). When applied to hydrophobic coal surfaces under certain conditions, polymer/surfactant solutions have proved useful in controlling dust in coal-cutting areas. This helps in reducing the risk of black lung disease in coal miners (8).

Polymer solutions have a high potential for use in enhanced oil recovery from underground reservoirs. Polymer flooding consists of adding a high molecular weight
polymer to the water of a waterflood to decrease its mobility (i.e., increase its apparent viscosity). The modes of use of polymers comprise:

a) Use of cross-linking agents in situ to cause gelation of the polymer and to effect a complete blockage of high conductivity zones.

b) The polymer solution slows the flow in high permeability regions due to its high apparent viscosity, thus avoiding "fingering" of the aqueous phase through the petroleum phase.

Several polymers have been used for polymer flooding: xantham and guar gums, hydrolyzed polyacrylamide (HPAM), copolymers of acrylic acid and acrylamide, hydroxyethylcellulose (HEC), carboxymethylhydroxyethylcellulose (CMHEC), polyacrylamide (PAM), polyethylene oxide (PEO) and polyvinyl alcohol (PVA).

Surfactants are also employed in enhanced oil recovery. They are used to alter the water/oil interfacial tension for displacing the oil that remains trapped by capillary forces. From the earliest days, it was recognized that capillary forces caused large quantities of oil to be left behind in well-swept zones of waterflooded oil reservoirs. Capillary forces are the consequence of the interfacial tension between the oil and water phases that resists externally applied viscous forces and causes injected water to bypass oil. Previous works have shown that certain polymer/surfactant mixtures exhibit a synergistic effect with regards to oil displacement; oil recovery is appreciably higher than with individual components (9,10). It is important to mention that since the water is usually a dilution of an oil-field brine, interactions with salinity must be considered (11).
1.2. Flow in Porous Media

In order to characterize the non-Newtonian aspects of flow in reservoirs, experiments in porous media have been and are currently developed (12). At this point, there are many aspects of the fundamentals of flow of polymer solutions through porous media that are not understood, which is part of the reason why polymer flooding has not been widely applied. Therefore, an understanding of the rheology of polymer and polymer/surfactant solutions in porous media aids in achieving specific technical goals, such as the suppression of fingering and the consequent increase in efficiency of oil recovery operations.

It is known that high molecular weight flexible polymers, such as PEO, flowing in porous media exhibit a viscosification that is dramatically affected by changes in their macromolecular conformation, associated with the formation of transient entanglements of the polymer molecules. Figure 1.2 shows typical curves of the resistance coefficient ($\Lambda$) vs. Reynolds number ($Re$), comparing Newtonian with polymer solution behavior. Such quantities are defined by:

\[
Re = \frac{udp}{\eta_s(1-\Phi)} \quad (1-1)
\]

\[
\Lambda = fRe \quad (1-2)
\]

The quantity $f$ is the friction factor and is calculated by:

\[
f = \frac{\Delta P d \Phi^l}{\Delta L \rho u^2 (1-\Phi)^2} \quad (1-3)
\]

Where:
\[ \frac{\Delta P}{\Delta L} \text{: Pressure drop per unit length} \]

d: particle diameter

\[ \Phi \text{: porosity of the medium.} \]

\[ \rho \text{: density of the fluid.} \]

\[ \eta_s \text{: viscosity of the fluid} \]

u: superficial velocity of the fluid

Figure 1.2. Typical behavior of flow resistance for Newtonian fluids and PEO solutions \((M_w = 8 \times 10^6)\) Values in the legend represent PEO concentrations \((13)\).

Figure 1.2 shows a departure from the Newtonian behavior for the polymer solutions, which is characterized by a sudden increase in flow resistance, at a specific value of the Reynolds number as well as by a dependence on polymer concentration. This phenomenon is directly related to the extensional nature of the flow at the pore level, and
is relevant to the selection of polymer flooding materials for enhanced oil recovery. Figure 1.3 illustrates the nature of the flow in a porous medium in which successive expansions and contractions produce extensional flow while, at the same time, there is extensive shear near the wall.

![Figure 1.3. Schematics of expansions and contractions that occur in porous media.](image)

Even though the flow field at the pore level is not an ideal extensional flow due to the relatively large velocity gradients close to the solid, the increase in flow resistance has been attributed to an extension thickening effect (14). The same principles of enhanced oil recovery can be considered for contaminant cleanup in aquifers (15).

1.3. Extensional Flows

Due to the importance of the extensional nature of the flow in porous media, it is of interest to study a flow field that is mostly extensional in nature. To accomplish this, an opposed-nozzle (opposed-jets) device is used. This system has been used extensively in the study of extensional flow fields (16-24). When fluid is sucked through two capillaries facing each other, a flow field that approximates uniaxial extension is generated, with a stagnation point (characterized by zero velocity) at the center of symmetry as shown in Fig. 1.4a. Figure 1.4b shows a picture of the flow field visualized by laser light scattered
at 90° from tracer particles.

Figure 1.4. (a) Diagram showing the opposed jets and the corresponding streamlines. (b) Flow field visualized by light scattered at 90° by tracer particles (this work).

1.3.1. Dilute Solutions. Extension of isolated chains

In opposed jets, the streamlines close to the stagnation point provide enough residence time for a fluid element such that isolated flexible polymer molecules subjected to a high enough strain rate can undergo a coil-stretch transition (25). Figure 1.5 shows an illustration of a stretching polymer molecule travelling on a streamline close to the stagnation point.
When the polymer coil is stretched, the hydrodynamic interactions between monomers decrease, and at the same time, the coil becomes more permeable to the fluid with a subsequent increase in friction. At this stage, a runaway stretching process occurs.

There are certain conditions that need to be satisfied in order for the coil-stretch transition to occur (26):

i. The extensional component must dominate over the rotational component.

ii. The molecule should be deformed at a critical strain rate ($\dot{\varepsilon}_c$) such that it exceeds its rate of relaxation ($1/\lambda$):

$$\dot{\varepsilon}_c \lambda > 1$$

(1)

iii. The coil should be exposed to $\dot{\varepsilon} > \dot{\varepsilon}_c$ for a long enough time so it can accumulate the required molecular strain.

Experimentally, the coil stretch-transition can be detected by measuring the intensity of the birefringence as a function of strain rate when a laser beam is passed through a region around the stagnation point located between crossed polarizers oriented ±45° with respect to the extension axis. The coil-stretch transition results in a narrow birefringent
line around the stagnation point of the flow (16). Figure 1.6 illustrates stagnation point between cross polarizers, and Fig. 1.7 shows the picture of a birefringent line for a PEO solution.

Figure 1.6. Diagram showing stagnation point between crossed polarizers and how light is polarized. The parameters $n_1$ and $n_2$ represent components of the index of refraction tensor. In this illustration, $n_1=n_2$, i.e., the medium is birefringent.
Further increases on strain rate lead to a broadening of the birefringent line up to a point where a dark central line appears. This occurs at a critical strain rate denoted by $\dot{\varepsilon}_p$, where $p$ stands for "pipe", since this is what the new birefringent pattern resembles. In this regime, early stretching of the polymer molecules causes an increase in extensional viscosity of the solution, which induces a change in the flow field characterized by a drop in the local strain rate around the stagnation point. The result is a return to the coil state of the polymer molecules and a consequent darkening of the birefringent line at the center. Figure 1.8 shows a picture of a typical birefringent pipe observed in PEO solutions.
1.3.2. Semi-Dilute Solutions. Formation of transient networks

Coil overlap in flexible polymer solutions theory occurs at a concentration denoted by $c^*$, representing the transition from dilute to semi-dilute solutions. This value is calculated assuming that the chains can be represented as spheres whose dimension is defined by the radius of gyration of the coil, and it corresponds to the concentration at which contact between spheres is established. For polymer concentrations above $c^*$, the polymer coils are able to interact with each other. Odell et al. (27) showed that on the time scale of $1/\dot{\varepsilon}$, the chains continue to extend as if in isolation irrespective of coil overlap. Up to this point the solution behaves as a dilute solution. When $\dot{\varepsilon}$ is increased beyond $\dot{\varepsilon}_c$, new effects set in beyond a specific concentration defined as $c^*$ (16). Once a critical strain rate is reached, there is a sudden increase in flow resistance along with a
delocalized birefringent pattern that can occupy the whole region between the jets. Such a pattern is called a "flare" since it resembles a flame in continuous motion. Figure 1.9 shows a picture of a flare pattern.

Figure 1.9. Picture of flare pattern. Observed at $\dot{\varepsilon} = 3000 \text{ s}^{-1}$ for a 1000 ppm PEO solution ($\bar{M}_w = 4 \times 10^6$) (this work).

The critical strain rate at which this event occurs is denoted by $\dot{\varepsilon}_n$, where $n$ stands for network. This value is a decreasing function of concentration and it decreases rapidly beyond $c^*$ and levels off at higher concentrations (16). The flare effect has been interpreted as a consequence of the formation of transient entanglements of polymer chains (17). The reason for this event to occur after certain strain rate lies on the fact that beyond $\dot{\varepsilon}_n$ (for times shorter than a characteristic time $\lambda_x$), an assembly of mutually overlapping chains can act as a mechanically connected network. In other words, the overlapping molecules do not have enough time to disentangle from each other before
undergoing extension. Figure 1.10 shows an illustration of polymer molecules that form entanglements while subjected to an extensional flow.

From extensional flow experiments it has been found that the concentration $c^-$ is lower than $c^*$ by a factor of 10-50, meaning that partly extended molecules start to overlap at concentrations much lower than $c^*$ (28).

The increase in flow resistance due to the presence of transient networks is revealed by an increase in pressure drop through the opposed jets (see appendix A for details) as $\dot{e}$ is increased. These transient entanglements are the cause of the extension-thickening behavior of solutions of flexible polymers in porous media flows (12). Even though a quantitative assessment of the extensional viscosity of the solution is not feasible with the opposed-jets system (29), the measure of pressure drops and the observation of birefringence patterns can be used to determine the average relaxation times of the polymer coils and transient entanglements. Figure 1.11 shows a typical curve of pressure drop as a function of strain rate comparing Newtonian behavior (water) with polymer
solution behavior. At a low PEO concentration, the pressure drop is slightly higher than that of water. At higher PEO concentrations, a sudden extension thickening occurs at a specific strain rate, which is the product of the formation of transient entanglements.

![Figure 1.11. Pressure drop as a function of strain rate for PEO solutions ($M_w = 4 \times 10^6$). Values in the legend represent PEO concentrations (note the similarities with the behavior in porous media, Fig. 1.2) (this work)](image)

1.4. Objectives and Outline of the Dissertation

The main objective of this work is to determine how the extensional flow of aqueous solutions of a high-molecular-weight poly(ethylene oxide) (PEO) is affected by the presence of anionic surfactants, using an opposed-jets device. It is well known that there is a strong connection between deformation at the molecular level and macroscopic rheology. Molecular deformation is effectively achieved by subjecting the polymer solution to uniaxial extension. As a result, the solution may exhibit extension thickening.
due to transient entanglements between molecules. The events that occur at the molecular level are very sensitive to the polymer conformation, and it is believed that an alteration of the natural PEO conformation in water due to the interactions with surfactants will have an effect on the macroscopic behavior of the fluid. Chapter II focuses on the interactions between PEO and sodium dodecyl sulfate (SDS). The study includes measurement of the extension-thickening behavior of the solutions and determination of strain rates required for the coil-stretch transition and the formation of transient entanglements in the semidilute regime. The effect of the presence of NaCl in solution is explored as well.

The presence of organic additives in water is known to affect the aggregation of surfactants. Chapter III presents results in the opposed-jets of PEO/SDS solutions to which n-alkanols have been added. Short and long-chain alcohols are used to account for the degree of hydrophobicity of the additive.

In Chapter IV, the rheological behavior of PEO is studied when the anionic surfactants have a different hydrophilic group. Sodium dodecyl benzene sulfonate (SDBS) and an α-olefin sulfonate (AOS) are the two surfactants under investigation. Both have a sulfonate group instead of a sulfate group (as does the SDS) and have longer alkyl chains than SDS as well. The interactions between PEO and surfactants with sulfonate groups have been barely explored, and here for the first time, experiments regarding the transient behavior of the solutions are also performed (Chapter V).

Finally, Chapter VI discusses theories on the behavior of dilute polymer solutions. The objective is to introduce the use of molecular theories to represent the rheological
behavior of polymer/surfactant solutions. First, some of the more traditional models are presented as well as comparisons between them, including a recent model by Lhuillier (30) that seems to offer some advantages over more well known approaches.
CHAPTER II

INTERACTIONS BETWEEN POLY(ETHYLENE OXIDE) AND SODIUM DODECYL SULFATE IN ELONGATIONAL FLOW

2.1. Introduction

It is well known that solutions of mixtures of certain polymers and surfactants can exhibit molecular interactions that might affect the rheological and physicochemical properties of the solutions. The nature of these interactions has been the subject of investigation for several decades (3). In particular, the interactions between poly(ethylene oxide) (PEO) and sodium dodecyl sulfate (SDS) in aqueous solutions have been extensively explored using techniques like surface tension (31,32), NMR (31,33-37), SANS (3,33,38), light scattering (39-41), conductimetry (32,42,43) and shear viscometry (38,42,44,45), among others. It is widely recognized that these interactions involve the formation of PEO/SDS complexes in which micellar aggregates attach to the PEO chain.

One of the proposed mechanisms for the formation of PEO/SDS complexes is depicted schematically in Fig. 2.1, along with observed variations in the shear viscosity of a PEO solution as SDS is added (38). The model proposed is based upon the notion that the electronegative nature of the PEO chain allows it to coordinate with the surfactant’s counterion (Na\(^+\)) to form a “pseudo-polycation” in which positive charges are distributed along the polymer coil (40,41,46). This charge distribution along the chain is not strong enough to produce an appreciable expansion of the coil in the absence of surfactant but it is enough to induce polymer/surfactant interactions.
At an SDS concentration that is below the concentration at which the surfactant begins to bind to the polymer molecules, the SDS and PEO molecules are dissolved without intermolecular interactions and the viscosity of the solution is not affected by the presence of surfactant (e.g., point 1 in Fig. 2.1). As the concentration of SDS in the solution increases, the concentration of sodium cations in solution also increases and the pseudopolyion is formed. At a specific SDS concentration (the Critical Aggregation Concentration - CAC, reported to be in the range 4.1-5.4 mM at 20°C), surfactant aggregates are formed along the polymer chains (point 2). For the PEO/SDS system, the CAC is substantially lower than the CMC (8.3 mM at 20°C). This fact is consistent with the mechanism proposed, since it is well known that the CMC of the surfactant decreases substantially as the ionic strength of the solution is increased by, for example, adding
NaCl. Once formed, the hydrophilic, negatively charged ends of the micellar aggregates associate with the positive charges along the PEO chain. In addition, there is evidence that a significant portion of the PEO chain exhibits hydrophobic interactions with the micellar aggregates (34,35,47), a fact that indicates that part of the chain penetrates into the aggregate. The contribution of the polymer coil to the hydrophobic effect by providing the surfactant with a nucleus for micellization has been cited in some cases as a major contributor to aggregate formation (48).

The micellar aggregates formed along the polymer chain are negatively charged, hence they repel each other and the polymer coils expand. As the surfactant concentration increases from the CAC, the surfactant added goes into the adsorbed micellar aggregates; the number of attached micellar aggregates also increases and the polymer coils keep expanding. This results in an increase in the solution viscosity (point 3 in Fig. 2.1). Eventually, a saturation point is reached at which the macromolecules have the maximum possible number of micellar aggregates attached. This is known as the Polymer Saturation Point (PSP). Presumably, the shear viscosity of the solution reaches a maximum at the PSP (point 4). As the concentration of SDS is increased beyond the PSP, the concentration of free Na\(^+\) increases substantially. These free cations can then shield the electrostatic repulsion between the SDS micelles, thereby causing a partial contraction of the coils and a reduction in shear viscosity. The fact that the addition of micellar aggregates to the chain and the electrostatic shielding balance exactly at the PSP, so that the shear viscosity curve reaches a maximum precisely at that point might be the subject of discussion. Since a well-defined plateau is typically not reached, one might
argue that both effects compete in a range of SDS concentrations around the PSP, so that the precise location of the PSP in the diagram shown in Fig. 2.1 does not have to coincide exactly with the maximum of the viscosity curve. However, Chari et al. (38) sustain, based on additional evidence, that the maximum corresponds to the PSP.

Both the CAC and the PSP have been reported to be independent of the PEO molecular weight, as long as it exceeds 5000 (42). However, there is limited evidence in the literature that suggests a slight effect of molecular weight (37).

The nature of molecular interactions around the PSP has been the subject of controversy. Some researchers (42,49) sustain that the polymer chain is first saturated with micellar aggregates and further addition of surfactant beyond that point results in a partitioning of surfactant molecules between micellar aggregates (thus increasing the aggregation number) and the bulk solution. Under this interpretation, the polymer chain becomes saturated with surfactant only when the intrinsic bulk concentration of surfactant reaches the CMC, i.e., further addition of surfactant beyond the PSP always results in the formation of free micelles (42,49). Other researchers (33,1) report that, after the PSP is reached, all the surfactant added dissolves as monomer in the bulk until the CMC is reached. Under this interpretation, there is a gap of surfactant concentration between the PSP and the formation of free micelles. More recently, Gjerde et al. (36) have reported that free micelles and aggregates might form simultaneously, indicating that free micelles occur below the true PSP. There is also evidence of PEO/SDS interactions at SDS concentrations well below the commonly reported values of the CAC (37).
Shear viscosity measurements such as those qualitatively represented in Fig. 2.1 usually have been performed by capillary (Ubbelohde) viscometry (42,50-52), although more recent works employ commercial rheometers with various geometries, such as cone and plate (44) and concentric cylinders (45). The latter techniques have the advantage that normal stresses can be measured and thus the viscoelasticity of the solution can be evaluated. Brackman (44) reported variations of the first normal stress difference of PEO/SDS solutions with SDS concentration that closely resemble the trends followed by the shear viscosity, with the difference that, at high shear rates and surfactant concentration, the normal stresses become almost independent of shear rate, a fact that Brackman attributes to shear-induced breakdown of PEO/SDS complexes.

Even though the shear behavior of PEO/SDS solutions has been extensively studied, flows with important elongational components have not been thoroughly investigated. Semi-dilute solutions of flexible polymers like PEO typically exhibit extension thickening in flow fields with appreciable elongational components, as opposed to their shear-thinning behavior in flows with prevalent shear components. Recently, Da Rocha et al. (53) conducted experiments with solutions of PEO/SDS mixtures flowing through porous media made up of disordered sphere packings. The combination of PEO with relatively small concentrations of SDS produces a modification of the extension-thickening behavior: in the presence of surfactant, apparent viscosities are appreciably higher than for the pure polymer solution, and the onset of extension thickening occurs at appreciably lower flow rates. These results are consistent with the changes in the apparent relaxation times brought about by changes in the shear viscosity of the solution.
However, at high ionic strengths (when the solvent is a 0.1 M NaCl solution), higher extension thickening effects were measured at relatively low SDS concentrations, despite the fact that the shear viscosities of the solutions were the same as those of equivalent PEO solutions in deionized water.

Recently, Eastman et al. (54) studied the extension-thickening behavior of polyvinylpyrrolidone (PVP)/SDS mixtures using an opposed-jet commercial rheometer (Rheometrix RFX). They also observed an enhancement of extension thickening in the presence of surfactant.

The opposed-jets system has been used extensively in the study of extensional flow fields (16-24). When fluid is sucked through two capillaries facing each other, a flow field that approximates uniaxial extension is generated, with a stagnation point at the center of symmetry. Streamlines close to the stagnation point provide enough residence time for the fluid elements so that isolated flexible polymer molecules (such as PEO molecules) subjected to a high enough strain rate undergo a coil-stretch transition. Experimentally, the coil stretch-transition is detected by measuring the intensity of the birefringence as a function of strain rate when a laser beam is passed through a region around the stagnation point located between crossed polarizers oriented ±45° with respect to the extension axis. The coil-stretch transition results in a narrow birefringent line around the stagnation point of the flow. For semi-dilute solutions, the visualization of birefringent patterns helps to ascertain when transient entanglement networks of polymer molecules are formed in the flow field. When transient entanglements are formed, a pattern is obtained with a delocalized, wide and unstable birefringent region that occupies...
the whole space between the capillaries. The onset of transient entanglements is also revealed by a sudden increase in the pressure drop across the jets as the strain rate is increased. These transient entanglements have been proven to be the cause of the extension-thickening behavior of solutions of flexible polymers in porous media flows (12). Even though a quantitative assessment of the extensional viscosity of the solution does not appear to be feasible to obtain with the opposed-jets system (12), the measure of pressure drops and the observation of birefringence patterns can be used to determine the average relaxation times of the polymer coils and transient entanglements.

In this work we will use the opposed-jets system to study how the formation of PEO/SDS complexes affects the elongational flow of solutions of a high-molecular weight PEO. The study includes measurement of the extension-thickening behavior of the solutions (through the measurement of pressure drops across the jets), and determination of the strain rates required for the coil-stretch transition of the complexes, and the formation of transient entanglements in the semi-dilute regime.

2.2. Experimental

A diagram of the experimental set up is shown in Fig. 2.2. The system is very similar to that used in previous works (18). The opposed capillaries have an internal diameter \( D = 0.55 \) mm, and a separation \( \delta = 1.2 \) mm. They are located at the center of a test cell with dimensions \( 2.5 \) cm \( \times \) \( 2.5 \) cm \( \times \) \( 10 \) cm, which ensures that the liquid is stagnant away from the region between the jets. The flow is induced by a vacuum pump that sucks the liquid from the feed reservoir, through the opposed jets, and finally into a receiving reservoir.
The fluid flow rate was measured as follows: the feed reservoir is connected to the atmosphere by a capillary tube of internal diameter lower than 0.44 mm and a length of 7 cm. As the liquid is being depleted from the bottom of the feed reservoir, the air flowing into the reservoir causes a pressure drop ($\Delta P_1$, measured by a pressure transducer) proportional to the flow rate of liquid ($Q$) going into the test cell. The pressure drop through the jets is recorded between a point in the test cell where the liquid velocity is negligible and the exit, by a second pressure transducer ($\Delta P_2$). Estimated values of pressure drop have been calculated for a Newtonian fluid using the mechanical energy balance (see Appendix A). The average strain rate in the extensional flow field is calculated by (for details see Appendix A):

$$\dot{\varepsilon} = \frac{4Q}{\pi D^2 \delta}$$  \hspace{1cm} (2-1)

A control program in the PC manipulates the solenoid valve to set the desired value of either pressure drop through the jets or measured strain rate. A steady state point is recorded once the measurements have stabilized. Typical experiments consist of a controlled increase of strain rate starting from rest. We also have performed experiments with controlled increase of pressure drop, and controlled decrease of pressure drop or strain rate. We report on the latter experiments at the end of the Results and Discussion section.

The birefringence around the stagnation point is visualized by a set up, also shown in Fig. 2.2, consisting of a 10 mW He-Ne laser, crossed polarizers and a $\lambda/4$ plate. A microscope at the end of the optical train is used to visualize the birefringence patterns. In
addition, the flow field in the region around the stagnation point is visualized by means of a microscope (not shown in Fig. 2.2) located at 90° with respect to the laser beam axis.

In the experiments, we measure the pressure drop and observe the birefringent patterns as a function of strain rate, varying the polymer and surfactant concentration, as well as the ionic environment of the solution. The PEO used was a polydisperse sample provided by Polysciences, with $\bar{M}_w = 4 \times 10^6$. The coil overlap concentration for this average molecular weight is estimated to be $c^* = 800$ ppm from intrinsic viscosity data (55). The surfactant used is a 99% pure Sodium Dodecyl Sulfate from Sigma-Aldrich. All the experiments were conducted at 20°C.

Figure 2.2. Schematics of the experimental setup. The inset represents the region between the opposed capillaries.
2.3. Results and Discussion

2.3.1. PEO Solutions

As a basis for comparison we present in this section pressure drops and birefringence observations for solutions of PEO in the absence of surfactant. The results presented here are qualitatively similar to those obtained with other high molecular weight samples of PEO (see Appendix B) in a different opposed jets system. (16,18)

![Pressure drop as a function of strain rate for PEO solutions. Values in the legend represent PEO concentrations.](image)

Figure 2.3. Pressure drop as a function of strain rate for PEO solutions. Values in the legend represent PEO concentrations.

Figure 2.3 shows pressure drops across the jets as a function of strain rate for solutions of various PEO concentrations, along with the curve obtained for pure water. At low PEO concentrations (100 and 250 ppm), the pressure drop is slightly higher than that
obtained for water. At higher PEO concentrations, a sudden extension thickening is observed at a specific strain rate. This extension thickening is the product of the formation of transient entanglements of polymer molecules in the flow field, as revealed by birefringence observations (see below). The onset strain rate for the extension thickening behavior decreases uniformly as the PEO concentration increases.

Figure 2.4 shows the 1000 ppm curve reported in Fig. 2.3, along with the birefringence patterns observed as the strain rate was increased: at low strain rates, no birefringence was observed. In this regime, the PEO molecules are in the coiled state and they do not exhibit interactions. At a specific strain rate, the polymer undergoes a coil-stretch transition, and a birefringent line appears around the axis of symmetry of the flow.
Further increases on the strain rate lead to a thickening of the birefringent line as molecules on streamlines farther away from the stagnation point are stretched. Eventually, the birefringent line darkens at the center, leading to what is termed a "pipe" pattern (16,17). In this regime, the increase in elongational viscosity of the solution brought about by the stretching of the PEO molecules causes a change in the flow field characterized by a drop in the local strain rate around the stagnation point with the consequent return to the coil state of the polymer molecules. The pipe pattern is commonly observed in this type of experiments, and its occurrence has been theoretically predicted by using a finitely-extensible nonlinear elastic dumbbell model (FENE), including nonlinear hydrodynamic friction for the evolution of polymer strains in the flow field (56). The stretch and pipe regimes do not produce a sizable increase in the pressure drop of the solution since the elongational viscosity increases and flow modification are confined to a relatively small region of the flow. As the strain rate is increased from the pipe regime, a point is reached at which the flow becomes unstable: the birefringence patterns become delocalized and unsteady, resembling a moving flare (16,17). At this point, a clear extension thickening effect is observed in the pressure drop curves. The flare regime is the product of the formation of transient entanglements of polymer molecules, and is characterized by the loss of the stagnation point: the flow becomes two parallel unstable converging streams flowing into each capillary (17). The formation of these transient entanglements occurs even below the coil overlap concentration (c*) because: (1) the statistical distribution of segments within a Gaussian coil implies that coil-coil interactions can exist at separations that are greater than $2 \times R_g$. 
where \( R_g \) is the radius of gyration of the coil; therefore, at short time scales the degree of interaction required for connectivity is much smaller since even tenuous entanglements will not be able to disentangle quickly enough \((16,28)\); (2) \( c^* \) is an average value for the polymer that does not reflect the coil size of the high end of the molecular weight distribution; and (3) after the molecules start to deform in the flow field, the effective coil size becomes much larger than that of the unperturbed coil, which favors interactions.

![Diagram showing the boundaries separating the birefringence patterns observed for PEO solutions. Each point corresponds to a different observation. The solid lines are smooth fits of the data points, shown to visualize trends. The vertical dashed line represents \( c^* \) (see text).](image)

The birefringence observations can be summarized in a diagram that shows the boundaries separating the various birefringent pattern regions. This is shown in Fig. 2.5 for the PEO solutions. In the scale shown, the coil-stretch transition strain rate is not appreciably sensitive to polymer concentration, but it shows a continuous decrease as
PEO concentration is increased, which is due to the increase in coil-solvent friction due to the increase in the shear viscosity of the solution. On the other hand, the onset of entanglements (pipe-flare transition) is very sensitive to PEO concentration. In fact, it is expected that at a sufficiently low PEO concentration this onset diverges to infinity. This limiting concentration \((c^*\approx 250\ \text{ppm})\), represented by the dashed vertical line in Fig. 2.5, represents the boundary between dilute and semi-dilute regimes for coils allowed to deform in the flow field. It was calculated by plotting the disentanglement time, \(\lambda_d = 1/\dot{\epsilon}_a\), where \(\dot{\epsilon}_a\) is the strain rate for the pipe-flare transition from Fig. 2.5, vs. \([\text{PEO}]\) and then extrapolating the concentration to \(\lambda_d = 0\).

2.3.2. PEO/SDS Solutions

The effect of surfactant addition to a solution of fixed PEO concentration (500 ppm) is shown in Fig. 2.6. At SDS concentrations of 5.0 mM and below, the results are identical to the pure PEO solution. This indicates a lack of significant interaction between the polymer and the surfactant. At SDS concentrations of 5.4 mM and beyond, a sizable effect on the extension thickening behavior is observed. Previous works have established that the CAC of the PEO/SDS system is in the range 4.1-5.4 mM (3). The results in Fig. 2.6 indicate that the formation of micellar aggregates along the PEO chains (which occurs at SDS concentrations higher than the CAC) decreases the onset for transient entanglement formation or, equivalently, increases the disentanglement time of the molecules. This increase in the disentanglement time can be the result of three different mechanisms. First, the presence of micellar aggregates along the chain causes coil
expansion due to electrostatic repulsions between micellar aggregates; second, the presence of the aggregates increases the effective volume of the chain, thus enhancing the possibility of chain overlap; and, third, a micellar aggregate attached to a chain can be a focus of interaction with a portion of a different chain. All three mechanisms imply increased intermolecular interactions in the presence of micellar aggregates and, therefore, an enhancement of extension thickening.

Figure 2.6. Pressure drop as a function of strain rate for PEO/SDS solutions at [PEO]=500 ppm. Values in the legend represent SDS concentrations.
Figure 2.7. Diagram showing the boundaries separating the birefringence patterns observed for PEO/SDS solutions for [PEO]=500 ppm. Solid lines have been drawn between data points to visualize trends. The indicated value of the CAC (4.5 mM) is an average of values reported in the literature.

A phase diagram corresponding to the 500 ppm PEO solution showing the various regimes of birefringence patterns is shown in Fig. 2.7, using as independent variable the SDS concentration. Below the CAC, there are no effects on the transitions. Beyond the CAC, the most dramatic effect is the reduction of the strain rate for the formation of transient entanglements (flare), which is consistent with the pressure drop results presented in Fig. 2.6. The coil-stretch transition strain rate is not appreciably affected by the formation of micellar aggregates, but this may be a consequence of a low sensitivity of the experimental observation. The stretch-pipe transition strain rate decreases appreciably beyond the CAC. This is an indication that the polymer/surfactant complex is capable of inducing flow modifications at lower strain rates, which is consistent with a
more pronounced effect on the extensional viscosity of the solution by the polymer/surfactant complex, as compared to the pure polymer. For SDS concentrations higher than 6.3 mM, birefringent lines and pipes were not observed; an increase in the strain rate always led to a loss of stability of the flow and formation of the flare pattern as the first evidence of birefringence in the flow. The lack of birefringent patterns before flare formation in this case may be a consequence of low sensitivity of the experimental observations.

According to the results in Figs. 2.6 and 2.7, the effect of surfactant addition is relevant up to an SDS concentration of 8.6 mM. The decrease in the strain rate for the onset of extension thickening seems to saturate at this point. This could be taken as an indication that the PSP has been reached. A number of previous works in which various techniques are used to study aggregate formation report the PSP as being equal to the concentration at which free micelles start to form (CMC*). A fit of literature data from various sources (31,32,36,43,48) yields the following dependence of the CMC* on the PEO concentration:

$$\text{CMC}^* = 8.2 + 5.5 \times 10^{-3} \text{ [PEO]}$$

with the CMC* in mM and [PEO] in ppm. This result is independent of PEO molecular weight beyond 5000, and it is consistent with data obtained by using a variety of experimental techniques. For a PEO concentration of 500 ppm, the calculated CMC* is 11.0 mM. The fact that the effect of the surfactant saturates at an appreciably lower concentration in our work might indicate that saturation is achieved at a lower SDS concentration. However, it may also be a result of the fact that the formation of transient
entanglements and the consequent extension thickening becomes less sensitive to the amount of surfactant attached to the polymer after a certain point. This would be consistent with an aggregation mechanism in which the number of micellar aggregates along the chain grows to a maximum well before the PSP is achieved. Further addition of surfactant beyond this point would increase the aggregation number of the attached clusters. Another aspect that needs to be considered is the possibility that the changes in chain conformation induced by the flow might affect the saturation process: the expansion of the coil in the extensional flow field could reduce topological hindrances for the formation of micellar aggregates along the chain, which could make it easier for the aggregates to form at lower bulk surfactant concentrations. However, our experimental technique does not allow us to reach a definitive conclusion in this matter.

The results obtained indicate that the extension thickening behavior of the PEO solutions is appreciably enhanced when the surfactant concentration exceeds the CAC. Fig. 2.8 shows results at a fixed SDS concentration (8.6 mM), for various PEO concentrations. A comparison with Fig. 2.3 shows the dramatic increase in extension thickening at this surfactant concentration. For instance, at a PEO concentration of 100 ppm, the PEO solution is practically indistinguishable from water (Fig. 2.3) whereas the solution with SDS exhibits pressure drops that reach more than five times those of water (Fig. 2.8). The extension thickening is a consequence of the formation of transient entanglements, as in the case of pure PEO, as revealed by birefringence observations.
Figure 2.9 shows the onset strain rate for entanglements ($\dot{\varepsilon}_n$) for pure PEO and PEO/SDS solutions at fixed SDS concentrations. Note that $\dot{\varepsilon}_n$ is reduced up to more than an order of magnitude for 8.6 mM SDS solutions as compared to pure PEO solutions. The 6.0 mM SDS solutions never saturate with micellar aggregates since their SDS concentration is lower than the CMC, which is the limiting PSP at low polymer contents. These solutions exhibit lower $\dot{\varepsilon}_n$ than the pure PEO solutions, but at high PEO concentrations, the amount of micellar aggregates per polymer chain decreases and the entanglement strain rate tends to get closer to that of pure PEO (Fig. 2.9). The 8.6 mM SDS/PEO solutions seem to exhibit two different regimes of change of $\dot{\varepsilon}_n$ with PEO
concentration, and the boundary between these two regimes coincides with the polymer saturation point: according to Eq. 2-2, 8.6 mM is the PSP of a solution with [PEO]=72 ppm. At PEO concentrations below the saturation point, the polymer chain is always saturated with surfactant aggregates, and $\dot{\varepsilon}_n$ exhibits a rapid change with PEO concentration. On the other hand, at PEO concentrations higher than the PSP, the proportion of micellar aggregates in the chain decreases as the PEO concentration is increased, since the solution moves farther away from the saturation point. This leads to a slower change of $\dot{\varepsilon}_n$. However, the $\dot{\varepsilon}_n$ values are still much lower than those obtained with the pure PEO. For very high PEO concentrations, we would expect the two curves to merge, following the trend observed for the 6 mM SDS solutions.

Figure 2.9. Strain rate required for transient entanglements for PEO and mixtures PEO/SDS.
Another interesting observation regarding the results shown in Figs. 2.8 and 2.9 is the dramatic reduction of $c$ in the presence of surfactant. For PEO solutions, $c$=250 ppm (Fig. 2.5). The extrapolated values of $c$ by letting the entanglements relaxation time go to zero for the PEO/SDS solutions in Fig. 2.9 cannot be determined accurately, but for both surfactant concentrations is below 5 ppm. This represents a reduction of around two orders of magnitude in the PEO concentration that represents the effective limit between the dilute and semi-dilute regimes under elongational flow. This reduction is a direct measure of the strength of interactions between polymer chains containing surfactant aggregates.

The purity of the SDS used may affect the results, as seen in Appendix C.

2.3.3. PEO/SDS in NaCl Solutions

It is well known that the CMC of SDS is lowered in the presence of NaCl (at 0.1 M NaCl, the CMC is 1.5 mM), and the aggregation number of individual micelles increases with salt concentration. Similarly, adding NaCl to PEO/SDS solutions lowers the CAC and increases the size and number of the micellar aggregates that attach to the polymer coil (3.43). This is an indication that stronger effects of surfactant presence are to be expected in solutions with NaCl. On the other hand, an excess of sodium ions in solution should screen the electrostatic repulsions between micellar aggregates attached to the polymer chain, thus reducing the degree of coil expansion. In spite of the electrolytic affinity of the dissolved PEO molecule, the presence of NaCl does not affect the extension thickening behavior of pure PEO solutions (12). In this work we have
conducted extensional flow experiments with PEO/SDS solutions dissolved in 0.1 M NaCl to assess the effects of the electrolyte on the extension thickening behavior of the solutions. Figure 2.10 shows pressure drop vs. strain rate for a fixed PEO concentration (500 ppm) and various surfactant concentrations. By comparing with Fig. 2.6, it can be seen that the effect of the surfactant on the extension thickening behavior starts to be significant at lower surfactant concentrations in the presence of NaCl. This was expected, in view of the lower CAC. A critical aggregation concentration of 1.0 mM has been reported for 0.1 M NaCl (43). The saturation of the surfactant effect also seems to occur at lower SDS content as compared to the solutions without salt, which is also consistent with PSP values reported in the literature; e.g., an extrapolation of results presented by Minatti and Zanette (43) yields a PSP of about 7.0 mM for 500 ppm PEO.

![Figure 2.10. Pressure drop as a function of strain rate for PEO/SDS solutions at [PEO]=500 ppm in 0.1 M NaCl. Values in the legend represent SDS concentrations.](image)

**Figure 2.10.** Pressure drop as a function of strain rate for PEO/SDS solutions at [PEO]=500 ppm in 0.1 M NaCl. Values in the legend represent SDS concentrations.
The shape of the pressure drop curves in Fig. 2.10 is appreciably different from those of the pure PEO solutions (Fig. 2.3) and PEO/SDS solutions (Fig. 2.6). The birefringence observations also indicate a qualitative difference in the nature of the flow. The different birefringence patterns observed in the presence of salt are illustrated in Fig. 2.11. At low strain rates, the observations show the appearance of a birefringent line (coil-stretch transition) and the onset of a pipe regime. In this case, the pipe formed in the flow field is typically thicker than that observed with pure PEO solutions. In the pipe regime, the extensive flow modification leads to a noticeable increase in the pressure drop. At a specific strain rate, the pipe pattern becomes unstable. As the strain rate is increased from
this point, the observations show an unstable and thick birefringent line. We will call this regime "unstable line". In this regime, the instabilities in birefringence patterns are limited to the region between the capillaries, as opposed to the flare pattern, in which birefringence is observed in regions relatively far from the stagnation point. In addition, the flow field in the flare regime is highly chaotic, to the point that the stagnation point is lost, whereas in the unstable line regime there is always a clear stagnation point. After the transition from the pipe to the unstable line regime, the rate of increase of pressure drop with strain rate decreases. This unstable flow pattern may be a consequence of the large increase of the extensional viscosity of the solution around the stagnation point, brought about by deformed PEO coils with relatively large attached micellar aggregates. An interesting observation is that the extension thickening produced by these flow instabilities tends to decrease in strength at higher strain rates, which may be a consequence of the reduction in the residence time of the molecules in the flow field. This observation is particularly relevant for the 2.9 mM SDS solution in Fig. 2.10, whose pressure drop tends to return to the pressure drop of the pure PEO solution at intermediate strain rates (4500-5000 s⁻¹). At higher strain rates, this solution exhibits an even more interesting behavior: while the pure PEO solution goes into the flare regime at 5300 s⁻¹, the flare in the 2.9 mM SDS solution is not attained until a strain rate of about 6000 s⁻¹, as revealed by birefringence observations. This behavior might be a consequence of intramolecular interactions in which a micellar aggregate interacts with two different portions of the polymer coil, which makes the formation of intermolecular cooperative structures (i.e., transient entanglements) more difficult, and thus requires a
higher strain rate for the occurrence of the flare pattern. The intramolecular interactions are caused by the screening of the electrostatic repulsion between micellar aggregates due to the presence of excess sodium ion in the solution. This type of behavior was previously observed in porous media flows of PEO/SDS/NaCl solutions (53), where at SDS concentrations slightly higher than the CAC, a delay in the onset of extension thickening was observed. A similar effect has been reported for elongational flows of aqueous hydroxypropyl guar in the presence of a cross-linking agent (57); at low enough polymer concentrations, intramolecular cross links inhibit extension thickening.

![Diagram showing the boundaries separating the birefringence patterns observed for PEO/SDS solutions for [PEO]=500 ppm in 0.1 M NaCl Solid lines have been drawn between data points to visualize trends. The dashed line indicates observations of transitions between the pipe and the unstable line regimes in which the flow instabilities were just barely perceptible and becoming more so as the SDS concentration approached the CAC.](image-url)

Figure 2.12. Diagram showing the boundaries separating the birefringence patterns observed for PEO/SDS solutions for [PEO]=500 ppm in 0.1 M NaCl Solid lines have been drawn between data points to visualize trends. The dashed line indicates observations of transitions between the pipe and the unstable line regimes in which the flow instabilities were just barely perceptible and becoming more so as the SDS concentration approached the CAC.
Figure 2.13. Pressure drop as a function of strain rate for PEO/SDS solutions in 0.1 M NaCl at [SDS]=4.1 mM for low PEO concentrations. Values in the legend represent PEO concentrations.

A map of the birefringence regimes for 500 ppm PEO solutions in 0.1 M NaCl is shown in Fig. 2.12. The decrease of the strain rate for the formation of transient entanglements (onset of the flare regime) at high SDS concentrations is as dramatic as that observed in the absence of NaCl (Fig. 2.7), but an increase in this strain rate is observed just above the CAC. As mentioned before, this is a consequence of intramolecular effects in which one micellar aggregate interacts with two different portions of the PEO chains. It is possible to envision these interactions when the amount of micellar aggregates attached to the chain is small, so that the PEO coil is not appreciably expanded. As the amount of aggregates increase, the electrostatic repulsion that expands the coil makes the intramolecular interactions more difficult and produces a
reduction in the strain rate necessary to form entanglements. It is interesting to note that both the coil-stretch and stretch-pipe boundaries in Fig. 2.12 also exhibit a slight maximum at intermediate surfactant concentrations. The unstable line regime extends over a wide area of the diagram, but it becomes gradually more difficult to observe as the CAC is approached, until it completely disappears at the CAC and below.

![Figure 2.14](image)

*Figure 2.14. Pressure drop as a function of strain rate for PEO/SDS solutions in 0.1 M NaCl at [SDS]=4.1 mM for high PEO concentrations. Values in the legend represent PEO concentrations.*

We also have explored the effect of polymer concentration for a fixed SDS concentration in the presence of NaCl. The results correspond to an SDS concentration of 4.1 mM. The pressure drop results are presented in Figs. 2.13 and 2.14, in two ranges of PEO concentrations. At low PEO contents (Fig. 2.13), the curves resemble those obtained without salt in the sense that the intermediate unstable-line region is not apparent.
(although birefringence observations confirm its existence for 250 ppm PEO, as discussed below). As the PEO concentration is increased up to 250 ppm, the onset of transient entanglements occurs at lower strain rates, and the extension thickening effect becomes more pronounced. However, at higher PEO concentrations (Fig. 2.14), an unexpected trend is observed: an increase in PEO concentration between 250 and 500 ppm leads to a weaker extension thickening. In the concentration range shown in Fig. 2.14, the unstable line region is evidenced by a lower rate of increase of the pressure drop at intermediate strain rates. The map of birefringence regime for these solutions is presented in Fig. 2.15. Local minima in transition strain rates are observed for the unstable line-flare transition and the pipe-unstable line transition.

![Graph](image-url)

**Figure 2.15.** Diagram showing the boundaries separating the birefringence patterns observed for PEO/SDS solutions for [SDS]=4.1 mM in 0.1 M NaCl. Solid lines have been drawn between data points to visualize trends.
In Fig. 2.16 we present comparisons of the strain rate for the formation of transient entanglements as the PEO concentration is varied for fixed surfactant contents. For the case of solutions with NaCl, the surfactant concentration of 4.1 mM is higher than the CMC and, therefore, it is expected to be the PSP corresponding to a certain PEO concentration. An extrapolation of data from reference (43) indicates that 4.1 mM SDS is the PSP for a PEO concentration of around 200 ppm. This value seems to coincide with the local minimum in the curve shown in Fig. 2.16. Below this PEO concentration, the polymer is always saturated with surfactant aggregates and seems to exhibit a rate of change of $\dot{\varepsilon}_n$ with PEO concentration similar to the case of PEO/SDS solutions without...
salt, which is not unlike that obtained for pure PEO. For PEO concentrations higher than 200 ppm (i.e., below saturation), as the relative amount of micellar aggregates per chain decreases, an actual increase in $\dot{\varepsilon}_a$ is observed. This indicates that the effect of micellar aggregates on the formation of entanglements weakens very rapidly as their number decreases. Eventually, the onset strain rate becomes very similar to that of the pure PEO and from this point onwards $\dot{\varepsilon}_a$ exhibits a decrease controlled by the PEO concentration. We would expect $\dot{\varepsilon}_a$ to become actually larger for the solution with salt, as intramolecular interactions start to appear, but this was out of the range allowed by our experimental set up under these conditions.

The results presented in this section indicate that the presence of NaCl affects significantly the extension thickening behavior of PEO solutions by providing stronger molecular interactions at the polymer chain level. When transient entanglements are formed, the rate of increase of pressure drops is higher in the presence of salt (Fig. 2.10) than for the case of pure PEO (Fig. 2.3) or PEO/SDS solutions (Fig. 2.6).

2.3.4. Effect of Experimental Protocol on Formation of Transient Entanglements

All the results presented so far correspond to an experimental protocol in which the strain rate of the solution was increased from rest to a specified value, controlled by the action of a solenoid valve. In this section we present representative results of experiments in which: (1) the controlled variable is the pressure drop, instead of the strain rate; and, (2) the experiment starts at a high value of strain rate and new steady states are obtained by decreasing the strain rate.
Our results show that the experimental protocol does not affect the pressure drop vs. strain rate curves or the boundary between birefringence patterns, except around the strain rates at which transient entanglements are formed, and only when the formation of transient entanglements leads to an abrupt change in pressure drops. An illustration of what is always observed is shown in Fig. 2.17 for a PEO solution. In the normal increasing strain rate mode, the pressure drop jumps abruptly when transient entanglements are formed (filled circles at about 3400 s⁻¹). This indicates that the onset of transient entanglements is a critical process that leads to a sudden increase in the apparent elongational viscosity of the solution (similar to a gelling point) so that to keep the solution flowing at the same rate of above, a much larger pressure drop is required. When the results are generated by increasing and controlling the pressure drop (void circles), after the strain rate reaches the onset of entanglements, further increases in the pressure drop result in a decrease in the strain rate. This is consistent with a sudden increase in the elongational viscosity. The effect becomes more noticeable as the criticality of the pressure drop jump increases. As an example, the inset in Fig. 2.17 shows a controlled-pressure drop curve of a mixture POE/SDS with NaCl with a steep pressure drop increase at the onset of transient entanglements (the controlled-strain rate curve for the same solution is shown in Fig. 2.10).

The fact that different steady states can be achieved at a specific pressure drop or strain rate suggests that a controlled-strain rate curve might exhibit hysteresis. This is indeed the case, as shown in Fig. 2.17: after getting to a point well within the flare regime, a controlled decrease in strain rates leads to a curve appreciably above to that
obtained increasing the strain rate. Transient entanglements survive until a strain rate of about 2800 s\(^{-1}\), which is substantially lower than that required for the onset of entanglements of the original curve. This hysteretic behavior might be a consequence of the modifications to the flow field exerted by the presence of transient entanglements: once the entanglements are formed and flow instabilities set in, the loss of the stagnation point decreases the residence time of the networks in the flow field and their disentanglement requires an appreciably lower strain rate.

![Graph](image)

**Figure 2.17.** Effect of experimental protocol on extension thickening for 750 ppm PEO solutions. A solid line has been drawn through the decreasing strain rate curve to better visualize its trend. The inset shows results for a solution with 500 ppm PEO, 6.0 mM SDS and 0.1 M NaCl.

### 2.4. Concluding Remarks

The formation of micellar aggregates of SDS along the PEO chain has a pronounced impact on the extension thickening behavior of the PEO solutions, especially with
regards to the formation of transient entanglements and their consequent increase in the apparent elongational viscosity of the solution. This happens for PEO/SDS and PEO/SDS/NaCl solutions. The limiting concentration at which entanglements occur drops substantially in the presence of aggregates as a consequence of the strengthening of interactions between PEO chains. This means that a PEO/SDS solution might exhibit intermolecular effects at concentrations that are orders of magnitude below the coil overlap concentration. The critical aggregation concentration agrees with values reported previously, which were obtained by means of different experimental techniques and with PEOs of appreciably lower molecular weights. On the other hand, for fixed PEO concentrations, as the surfactant concentration is increased, the saturation of the effect of the surfactant occurs at lower concentrations than previously reported. This might be the consequence of a decreased sensitivity of the elongational viscosity to the number and distribution of micellar aggregates along the polymer chain as the saturation point is approached. Since the enhancement of extension thickening by micellar aggregates along the PEO chain is a consequence of coil expansion and the strengthening of intermolecular entanglements, it is reasonable to speculate that the magnitude of the effect will be more significant as new micellar aggregates are added to the chain (i.e., at surfactant concentrations higher than but close to the CAC) than close to the saturation point.

In the presence of an excess of NaCl, the increases in pressure drop observed when extension thickening occurs are noticeably larger than those obtained for PEO/SDS aqueous solutions. This indicates that intermolecular interactions between PEO chains are stronger in the presence of electrolyte, which might be a consequence of the larger size of
micellar aggregates. On the other hand, at concentrations of SDS just beyond the CAC, intramolecular effects are noticeable, and their main consequence is a reduction of the extension thickening effect.
CHAPTER III

ELONGATIONAL FLOW OF SOLUTIONS CONTAINING POLY(ETHYLENE OXIDE)/SODIUM DODECYL SULFATE COMPLEXES IN THE PRESENCE OF n-ALKANOLS

3.1. Introduction

Under certain conditions, a surfactant added to a polymer solution can form micellar aggregates that associate with the polymer molecules. This aggregation process influences the physicochemical characteristics of the solution, as well as its rheological behavior. One of such interacting systems that has been studied thoroughly is the mixture of poly(ethylene oxide) (PEO) and sodium dodecyl sulfate (SDS) in aqueous solutions. It has been reported widely that SDS micellar aggregates are formed along the PEO chain at SDS concentrations higher than the Critical Aggregation Concentration (CAC), reported to be in the range 4.1–5.4 mM at 20°C, which is substantially lower than the critical micelle concentration (CMC) of the surfactant (8.3 mM at 20°C) (3).

From a rheological standpoint, previous works have concentrated on the use of shear rheometry to determine the viscosity of PEO/SDS solutions (38,42,44,45,50,52). The formation of SDS micellar aggregates along the PEO chain leads to an increase of the shear viscosity of the solution, which has been explained as being a result of PEO coil expansion, brought about by the repulsion between negatively-charged micellar aggregates attached to the PEO chain. The shear viscosity increases as the SDS concentration is increased from the CAC, until it reaches a maximum when the polymer molecules saturate with micellar aggregates (38). The SDS concentration at saturation is termed the Polymer
Saturation Point (PSP).

In elongational flows, solutions of high-molecular weight PEO exhibit extension thickening, i.e., the apparent viscosity of the solution increases as the strain rate is increased. One way of creating a nearly ideal elongational flow is by sucking fluid through two opposed capillaries. This is the so-called opposed-jets system, where a flow field resembling uniaxial extension can be created. The opposed-jets system has been used extensively in the study of elongational flows of polymer solutions (16,21). Pressure drops vs. strain rate curves for aqueous solutions of a high molecular weight PEO are shown in Fig. 3.1 for flow between opposed jets as a function of polymer concentration (58).

![Graph showing pressure drop vs. strain rate for PEO solutions](image)

Figure 3.1. Pressure drop in opposed jets (internal diameter: 0.55 mm, jets separation: 1.2 mm) as a function of strain rate for PEO solutions ($\bar{M}_w=4\times10^6$). Values in the legend represent PEO concentrations (58).
Figure 3.2. Pressure drop changes of the 1000 ppm PEO solution \( \left( \overline{M}_w = 4 \times 10^6 \right) \) in Fig. 3.1, showing all the observed birefringence patterns and their range of occurrence. The solid line corresponds to water.

Figure 3.2 details the birefringence patterns observed between crossed polarizers for the 1000 ppm curve in Fig. 3.1, a solution that is semi-dilute since its concentration is above that for coil-coil overlap. At low strain rates, the highly flexible PEO molecules are in a coiled state and the solution is optically isotropic. As the strain rate is increased, the polymer undergoes a coil-stretch transition, and a birefringent line appears around the axis of symmetry of the flow. The polymer coils only stretch appreciably along streamlines close to the stagnation point, on which the residence time is long enough. For this reason, pressure drops do not increase appreciably with respect to water. Further increases of the strain rate lead to a thickening of the birefringent line, which darkens in the center in what
has been termed a "pipe" pattern. In this regime, the increase in the elongational viscosity
of the solution around the axis of symmetry produces a change in the flow field that allows
the molecules to relax back to the coil state. Note that a slight degree of extension
thickening is observed in the pipe pattern, as revealed by the increase in the pressure drop.
As the strain rate is further increased, the flow becomes unstable, the birefringence
patterns become delocalized and unsteady. This is the "flare" regime, in which a
substantial increase in pressure drop is observed, caused by the formation of transient
entanglements of polymer molecules.

![Graph showing pressure drop vs. strain rate](image)

Figure 3.3. Pressure drop in opposed jets as a function of strain rate for PEO/SDS solutions
at [PEO]=500 ppm (Mw =4x10^6). Values in the legend represent SDS concentrations.

The changes of polymer conformation in the presence of micellar aggregates have a
dramatic effect on the extension thickening of PEO solutions, as revealed by our previous
work on porous media flows (53) and flow in opposed jets (58). Figure 3.3 shows pressure drop across opposed jets for a fixed PEO concentration as the SDS concentration is increased. The results correspond to the same system reported in Fig. 3.1. The presence of surfactant starts affecting the pressure drops at concentrations between 5.0 and 5.4 mM, which indicates that the CAC is within this range. The onset strain rate for the formation of transient entanglements is decreased by more than an order of magnitude before saturation of the PEO chains by micellar aggregates is achieved.

The reduction of the onset strain rate for transient entanglements when micellar aggregates are present indicates an increase in the degree of intermolecular interactions between polymer molecules. Three effects might contribute to the increased level of interactions: the coil expansion produced by the electrostatic repulsion between micellar aggregates, the increase in the effective volume of the chain by the presence of attached aggregates, and intermolecular interactions between two or more different PEO chains that can be attached to the same micellar aggregate (i.e., bridging of PEO chains through SDS micelles). Note that the effect of the micellar aggregates on the pressure drop curves varies gradually with SDS concentration between the CAC and the saturation point. This is due to the increase in the number and size of attached micellar aggregates with SDS concentration.

A significant practical implication of the results in Fig. 3.3 is the possibility of controlling the strain rate required for transient entanglements and the apparent extensional viscosity of the PEO solution, by attaching micellar aggregates to the polymer molecules. The extent of the effect is set by the SDS concentration, which
represents the only degree of freedom in this system. However, the size of the micellar aggregates and their distribution can be modified by the presence of additives. For instance, additives such as electrolytes and organic compounds are known to have a significant effect on the CMC, CAC and micelle aggregation number and shape. The presence of an electrolyte causes the CMC of SDS and the CAC of SDS/PEO to decrease, due to the screening of the ionic atmosphere surrounding the ionic head groups by dissolved counterions (59). It is also known that the addition of NaCl to PEO/SDS solutions increases the size and number of micellar aggregates that attach to the polymer chain (3,43). In elongational flows, this has consequences that depend on surfactant concentration: at SDS concentrations slightly higher than the CAC, the extension thickening effect is delayed to higher strain rates due to the contraction of the PEO coil produced by intramolecular interactions within the PEO chain induced by the presence of micellar aggregates. At higher SDS concentrations, the extension thickening effect is strengthened with respect to solutions without salt: pressure drops are much higher and increases of pressure drop with strain rate are more abrupt once transient entanglements set in (58).

Other types of additives affect micellization of SDS in aqueous solutions. For instance, the effect of alcohols has been widely studied (60). Changes in SDS micellization in the presence of alcohols are due to changes in the solvent hydrophobicity and to the fact that alcohols are solubilized in the micelles, changing their structure (61). The changes induced by alcohols are found to depend strongly on alcohol molecular structure and concentration. Short-chain alcohols (four or less carbon atoms) are soluble in water and
are simultaneously solubilized within SDS micelles (61). In the micelle, short-chain alcohols are located near the ionic shell, which reduces the electrostatic repulsion and lowers the CMC at low alcohol contents (3,60). However, relatively high concentrations of short-chain alcohols increase the solvent hydrophobicity, which results in an increase of surfactant solubility (as monomer) and an increase of the CMC (60): adding high concentrations of a short-chain alcohol to a micellar solution decreases the micellar aggregation number (61-63) and ultimately dissolves the micelles (64,65). On the other hand, long-chain alcohols, whose solubility in water is relatively small, partition favorably inside the micelles and always lower the CMC (60,63).

For the series of n-alkanols, at a fixed alcohol concentration, the SDS micellar aggregation number decreases as the alkyl chain length increases, reaching a minimum for pentanol, and then it increases from pentanol to octanol (63). The minimum becomes more pronounced as the alcohol concentration is increased. At the same time, the number of alcohol molecules within a micelle increases uniformly with alcohol chain length (62,63). At low alcohol concentrations, trends in the micelle volume are controlled by the SDS aggregation number: appreciable swelling of the micelles is only observed for long-chain alcohols (n-heptanol and n-octanol). The effect of alcohol concentration is more complex: for n-heptanol and n-octanol, SDS aggregation numbers increase uniformly with alcohol concentration whereas for shorter-chain alcohols they tend to decrease.

The effect of n-alkanol/SDS interactions has been studied also from a rheological standpoint. For n-hexanol, shear rheometry has shown that, at low surfactant contents, the shear viscosity increases only marginally with the concentration of n-hexanol, which has
been interpreted as the result of a small increase in micellar volume as n-hexanol becomes solubilized (66). Above a certain concentration, n-hexanol is also solubilized in the micelle interior producing swollen micelles, presumably of spherical shape as confirmed by quasielastic light scattering. At higher SDS concentrations, above a specific n-hexanol concentration, there is a shape transition from spherical to rod- or disc-like micelles.

Similar results to those quoted above have been obtained with n-octanol (67). The n-octanol/SDS system has two aggregation steps: a low-concentration transition (CMC) that gives isometric (spherical or ellipsoidal), almost fully-ionized micelles, and a higher-concentration transition that corresponds to a shape change to anisometric micelles. The total aggregation number increases as the concentration of n-octanol increases, producing larger alcohol-surfactant mixed micelles. This behavior agrees with previous results with n-octanol (62) and with n-butanol, n-pentanol and n-hexanol in the absence (68) and the presence of salt (69).

The works mentioned above involve n-alkanol/SDS interactions in the absence of PEO. However, we expect the same trends to be followed in the presence of PEO. This is confirmed by studies conducted with n-butanol in PEO/SDS solutions (70). The addition of n-butanol to PEO/SDS solutions decreases the CAC and the concentration at which free SDS micelles start to appear, and solubilization of n-butanol into micellar aggregates starts occurring at the CAC.

The observations discussed above indicate that the structure of SDS micelles can be manipulated, to a certain extent, by the addition of n-alkanols. From the point of view of increasing the extension-thickening potential of PEO solutions, long-chain alkanols seem
to be the best choice, since their main effect would be due to comicellization with SDS. In this work, we use the opposed-jets device to study how the presence of short and long chain alcohols: ethanol and n-octanol affects the rheological behavior of solutions of PEO/SDS mixtures in elongational flows.

3.2. Experimental

A schematic diagram of the experimental set up is shown in Fig. 3.4. The apparatus is the same used in previous investigations (58). Two different sets of opposed capillaries were used. The capillaries in one set (jets 1) have an internal diameter \( D = 0.55 \) mm, and a separation \( \delta = 1.2 \) mm. The capillaries in the second set (jets 2) have \( D = 0.60 \) mm, and \( \delta = 1.2 \) mm. The two sets yield somewhat different pressure drops for pure water, but the results presented in this work are not appreciably affected by capillary size. Both jets 1 and jets 2 are located at the center of a test cells with dimensions 2.5 cm x 2.5 cm x 10 cm, which ensures that the liquid is stagnant away from the region between the jets. The flow is induced by a vacuum pump that sucks the liquid from the feed reservoir, through the opposed jets, and finally into a receiving reservoir. The fluid flow rate was measured by monitoring the pressure drop through a small capillary (\( \Delta P_1 \), measured by a pressure transducer) that lets air into the feed reservoir at a volumetric rate equal to the liquid flow rate through the jets. The pressure drop through the jets is recorded between a point in the test cell where the liquid velocity is negligible and the exit, by a second pressure transducer (\( \Delta P_2 \)). The average strain rate in the extensional flow field is calculated by

\[
\dot{\varepsilon} = \frac{4Q}{\pi D^2 \delta}
\]  

(3-1)
where $Q$ is the total volumetric flow rate going through the jets.

A control program in the PC manipulates the solenoid valve to set the desired value of strain rate. A steady state point is recorded once the measurements have stabilized. All the experiments consist of a controlled increase of strain rate starting from rest. Previous work (58) has shown that pressure drop vs. strain rate curves might exhibit hysteresis, depending on how the flow is set.

The birefringence around the stagnation point is visualized by an optical train consisting of a 10 mW He-Ne laser, crossed polarizers and a $\lambda/4$ plate. A microscope at the end of the optical train is used to visualize the birefringence patterns.

Figure 3.4. Schematics of the experimental setup. The inset represents the region between the opposed capillaries.
In the experiments, we measure the pressure drop and observe the birefringent patterns as a function of strain rate, varying the polymer, surfactant and alcohol concentrations. Two different PEOs were used; both were polydisperse samples provided by Polysciences, with $M_w = 4 \times 10^6$ and $M_w = 8 \times 10^6$. The lower molecular weight polymer was used in mixtures with n-octanol and 99% pure SDS, obtained from Sigma-Aldrich, whereas the higher molecular weight polymer was used in mixtures with various alcohols and 95% pure SDS, obtained from J.T. Baker. Experiments conducted with the same polymer sample and SDS in the 95-99% purity range showed no effect of the type of SDS. The alcohols used were analytical-grade samples obtained from Sigma-Aldrich, Riedel-de-Häen and Fischer. All the experiments were conducted at 20°C.

3.3. Results and Discussion

The use of short-chain alcohols to modify the structure of SDS micellar aggregates along PEO chains is expected to require high alcohol concentrations because of their high solubility in water, and the consequent partitioning of the alcohol between the micelles and the solution. Relatively high alcohol concentrations will change the properties of the solvent in which the polymer chains are dissolved and this, in turn, might affect the elongational flow behavior of the polymer solutions. To explore this effect, we have performed experiments with a fixed PEO concentration and various ethanol concentrations in the absence of surfactant. Typical results are shown in Fig. 3.5. For this PEO molecular weight and concentration (15 ppm), the polymer solution behavior barely differs from that of water, but when ethanol is added, increasing degrees of extension thickening are
observed as the ethanol concentration is increased. Specifically, the onset strain rate for molecular entanglements gets to be as low as 1400 s\(^{-1}\) (25\% ethanol), whereas for pure water as a solvent, no transient entanglement formation is observed up to \(\dot{\varepsilon} = 7000\) s\(^{-1}\).

![Pressure drop in jets 2 as a function of strain rate for PEO/ethanol solutions at \([\text{PEO}]=15\) ppm (\(\overline{M}_w = 8\times10^6\)). Values in the legend represent ethanol concentrations (71).]

It is known that ethanol/water solutions are poorer solvents than pure water for PEO (72). This would cause a coil contraction upon the addition of ethanol that would result in higher relaxation times and, consequently, higher strain rates would be required for a coil-stretch transition if the solution is in the dilute regime. On the other hand, in this concentration range, addition of ethanol to water produces an increase in viscosity: at 20°C, a 25\% ethanol solution has a viscosity that is more than twice that of water. A higher viscosity would reduce the strain rate required for coil stretch transition or transient
entanglements, due to the increase of friction between the solvent and the polymer molecules. The poorer solvency and viscosity effects should counteract. However, the results shown in Fig. 3.5 indicate a reduction in onset strain rates that surpasses that expected by viscosity increases. These results suggest stronger interactions than expected between polymer chains in the presence of ethanol. This behavior has been observed in measurements of shear viscosity of PEO/ethanol aqueous solutions (72), for which shear thinning is much stronger in the presence of ethanol. This observation has been explained in terms of a preference of the PEO chains to form polymer-polymer contacts over solvent/chain contacts in a poorer solvent. Thus, for solutions of sufficiently high PEO concentration (i.e., semi-dilute solutions), formation of transient entanglements are promoted by the presence of ethanol.

![Figure 3.6. Pressure drop in jets 2 as a function of strain rate for PEO solutions at [PEO]=15 ppm ($M_w=8x10^6$), and 5% v/v ethanol concentration (71).](image)
Figures 3.6, 3.7 and 3.8 show the effect of adding ethanol at three different concentrations on the opposed-jets flow of PEO/SDS mixtures. The SDS concentration in Figs. 3.6 and 3.7 (8.2 mM) is high enough that micellar aggregates have a large effect on the solution: a 15 ppm PEO solution is indistinguishable from water at strain rates lower than 3000 s$^{-1}$, as seen in Fig. 3.5, whereas the PEO/SDS solution exhibits extension thickening from very low strain rates. A concentration of 5% ethanol (Fig. 3.6) does not seem to be high enough to alter the polymer-surfactant interactions, even though it has some effect when the surfactant is absent (Fig. 3.5). At a 15% level (Fig. 3.7), the ethanol increases the onset strain rate for extension thickening of the PEO/SDS solution. Short-
chain alcohols in aqueous solutions of SDS can break micelles due to the increased hydrophobicity of the solvent. A reduction in the number of micellar aggregates would explain a weaker extension thickening, such as that observed in Fig. 3.7.

\[
\Delta P \text{(kPa)}
\]

\[
\dot{\varepsilon} \text{ (s}^{-1}\text{)}
\]

Figure 3.8. Pressure drop in jets 2 as a function of strain rate for PEO/ethanol solutions at [PEO]=15 ppm (\(M_w=8\times10^5\)), and 25% v/v ethanol concentration. Values in the legend represent SDS concentrations (71).

The results in Figs. 3.6 and 3.7 indicate that, at such low ethanol contents, the micellar aggregates control the solution rheology to the extent that the alcohol does not even exert the same effect that it produces on the pure polymer solution (Fig. 3.5). On the other hand, at higher ethanol contents, this trend is reversed. Figure 3.8 shows results for 25% ethanol and several SDS concentrations. The results indicate that addition of SDS does not contribute to the extension thickening of the polymer solution when ethanol is present.
in this proportion. In this case, ethanol controls the extension thickening of the PEO. We believe that this effect results from the inhibitory influence that the high concentration of ethanol has on the formation of micellar aggregates: a 25% solution of ethanol in water has a CMC for SDS of 12.5 mM (60). Even though the CAC is expected to be lower, the SDS concentrations in Fig. 3.8 are all below the CMC, so that it seems reasonable to assume that no appreciable number of micellar aggregates are present in this range.

The results presented above show that ethanol either promotes extension thickening, as observed for a pure semi-dilute PEO solution, or weakens the extension thickening gained by adding SDS to PEO solutions. The main effect is related to the properties of ethanol as a co-solvent either for PEO or for SDS, and the inclusion of ethanol in the micellar aggregates has no measurable effect. Therefore, relatively large concentrations of ethanol (more than a few percent) are needed to observe an effect, since the solvent quality needs to be changed, and, as a consequence, a prediction of the solution performance in elongational flows becomes very complex.

An increase in the alkyl chain length of the alcohol should make co-micellization more of a factor, and should reduce the concentration at which the alcohol presence will have an effect. This is indeed the case, as illustrated in Fig. 3.9, where results corresponding to the addition of various alcohols at low concentrations to a PEO/SDS solution are presented. Short-chain alcohols have no effect at such low concentrations, but the effect of n-octanol is dramatic: at a concentration of 2.9 mM (0.05% v/v), the extension thickening is greatly enhanced for a PEO/SDS solution that is at an SDS concentration below the CAC of the
PEO solution, i.e., n-octanol has promoted the formation of micellar aggregates along the PEO chain. The n-octanol concentration might seem very low, but it is important to mention that the solubility of n-octanol in pure water is barely 3.7 mM at 20°C. At this level of concentrations, we found no effect of addition of n-octanol on the behavior of pure PEO solutions (results not shown). This is not surprising since the concentration is too low to exert any influence on the solvent quality with regards to PEO macroconformation.

It is known that n-octanol produces a decrease in the CMC of SDS, and that it micellizes with the SDS to form micelles with aggregation numbers and sizes that increase with n-octanol concentration (62,67). In what follows, we will analyze the effect
of n-octanol over the extension thickening of PEO/SDS solutions.

Figure 3.10 shows results for fixed polymer and surfactant concentration (500 ppm and 5.4 mM, respectively) at various concentrations of n-octanol. The PEO/SDS system is barely beyond the CAC (Fig. 3.3) but micellar aggregates have a definite effect on the extension thickening of the solution without alcohol. The results show that, as the concentration of n-octanol is increased, the critical strain rate for transient network formation ($\dot{\varepsilon}_n$) is progressively decreased, indicating that addition of n-octanol promotes intermolecular interactions between polymer chains. Three different mechanisms might contribute to this behavior: (1) As the n-octanol concentration increases, we expect the
CAC of the surfactant to decrease, following the trends observed for the CMC in the absence of polymer. This implies that more of the free surfactant molecules might associate to form mixed micellar aggregates along the PEO chain as the amount of alcohol in solution is increased; (2) it is expected that the micellar aggregates that attach to the polymer chain increase their aggregation number as more n-octanol is added, as free micelles do; and (3) mixed SDS/n-octanol micelles have a lower surface potential than SDS micelles (67) so that the mixed aggregates will not repel each other as strongly as pure SDS aggregates, which means that more aggregates per chain are potentially possible, which would strengthen interchain interactions.

The effect of n-octanol on pressure drop curves for the results in Fig. 3.10 saturates at a concentration between 3.2 and 5.0 mM. Note that 5.0 mM n-octanol is higher than the solubility in pure water. The fact that this excess alcohol has dissolved means that mixed micelles of SDS/n-octanol are being formed. The saturation of the effect implies that further additions of n-octanol are not affecting the micellar aggregates along the PEO chain to an extent that is measurable in these experiments. It is interesting to observe that the curve corresponding to 5.0 mM n-octanol is identical to the curve corresponding to 500 ppm PEO and 8.6 mM SDS in Fig. 3.3, for which the effect of SDS on the pressure drop curves has saturated. This result suggests that mechanism (1) proposed above might be the dominant effect in the enhancement of extension thickening by n-octanol: once the PEO saturates with micellar aggregates, the results are the same, independently of the means used to achieve saturation.
To further explore this point over a wider range of strain rates (note that the pressure drop curves at saturation in Fig. 3.10 span a short range of $\dot{\varepsilon}$), we prepared solutions at lower PEO concentrations (20 and 35 ppm) with an SDS concentration at which the effect of SDS has saturated (8.6 mM) and varied the n-octanol concentration between 0 and 5.0 mM. Typical results are shown in Fig. 3.11 (any solution below 100 ppm of this PEO in absence of SDS is indistinguishable from pure water, see Fig. 3.1). We found that the addition of n-octanol did not affect the extension thickening behavior in all cases. According to measurements reported by Moya and Schulz (67), an aqueous solution with 8.6 mM SDS and 5.0 mM n-octanol would have mixed micelles containing around 50
molecules of SDS and 70 molecules of n-octanol (micelles of pure SDS would contain around 60 molecules of surfactant). Hence, even though the micelle composition has changed substantially upon addition of n-octanol, the extension thickening behavior has not been affected. This suggests that the most important factor determining changes in extension thickening due to the presence of micellar aggregates along the PEO chain is the number of aggregates and not their composition.

The effect of addition of n-octanol to PEO/SDS solutions without micellar aggregates is shown in Fig. 3.12. The SDS concentration (4.0 mM) is below the CAC and the results are the same as without SDS (Fig. 3.3). Low n-octanol concentrations (0.5 mM) do not
exert an appreciable change, but after a certain n-octanol content is reached (presumably the n-octanol concentration that lowers the CAC to 4.0 mM), a definite enhancement of the extension thickening is observed until saturation is reached. The same qualitative trends are observed with the high molecular weight PEO at a much lower PEO concentration (Fig. 3.13). Note that, in this case, the PEO solution is indistinguishable from pure water and the CAC has been surpassed, as evidenced by the enhancement in the extension thickening of the PEO/SDS solution.

Figure 3.13. Pressure drop in jets 2 as a function of strain rate for PEO/SDS/n-octanol solutions at [PEO]=15 ppm ($\overline{M}_w=8\times10^5$), [SDS]=4.7 mM. Values in the legend represent n-octanol concentrations.
Figure 3.14 shows the effect of n-octanol on the boundaries between regions with different birefringence patterns corresponding to the results shown in Fig. 3.10. The coil-stretch transition strain rate is not appreciably affected by the increase in the number of mixed micellar aggregates, and the stretch-pipe transition strain rate only decreases slightly. For n-octanol concentrations higher than 1.5 mM neither birefringent lines nor pipes were observed. The continuous decrease of the strain rate for onset of transient entanglements (or flare pattern) indicates that even a small amount of n-octanol induces changes in the structure of the PEO/SDS complex. This is not the case for the 4.0 mM SDS solutions. Figure 3.15 shows the onset strain rates for transient entanglements ($\dot{\varepsilon}_t$)
for both the 5.4 and 4.0 mM SDS solutions. The 4.0 mM SDS solution requires that a certain amount of n-octanol be added before micellar aggregates attach to the PEO chain. As discussed above, that n-octanol concentration would be the one necessary to lower the CAC of the surfactant to 4.0 mM. It is interesting to note that, in terms of the representation presented in Fig. 3.15, for a fixed SDS concentration, one could define an n-octanol "CAC" that would be between 0.5 and 1.0 mM.

![Graph](image)

Figure 3.15. Strain rate required in jets 1 for transient entanglements for mixtures of PEO/SDS/n-octanol at [PEO]=500 ppm (M_w =1x10^6). Values in the legend represent SDS concentrations.

The depression of the true CAC for the surfactant and its influence on $\dot{\varepsilon}_w$ are better seen in Fig. 3.16, where the effect of SDS concentration is presented in absence of n-octanol and with a relatively high concentration of n-octanol, 3.7 mM (which corresponds
to its solubility in pure water). It is interesting to notice that the effect of n-octanol is so dramatic that the apparent saturation is reached approximately at a concentration where aggregation of SDS has not even started in the absence of alcohol.

![Diagram showing strain rate vs. SDS concentration](image)

**Figure 3.16.** Strain rate required in jets for transient entanglements for mixtures of PEO/SDS/n-octanol at [PEO]=300 ppm ($M_w=10^6$). Values in the legend represent n-octanol concentrations.

In Fig. 3.17, we have sketched the CAC values obtained for our two polymers in the same plot with the CMC values reported by Moya and Schulz (67). After the sharp drop in the CMC at low n-octanol concentrations, the CMC and the CAC are comparable; i.e., the addition of n-octanol shortens the gap between the CMC and the CAC. A similar trend has been observed for the SDS/n-butanol system (70). From this observation, it can be concluded that n-octanol is a strong promoter of micellar aggregation, to the point that in
its presence, the hydrophobic effect introduced by the presence of PEO does not contribute notoriously to the formation of the aggregates.

The results presented above show that relatively small concentrations of n-octanol (of the order of 0.05% or less) can substantially decrease the onset of extension thickening of PEO/SDS solutions with significantly lower amounts of PEO than those needed in the absence of n-octanol.

![Figure 3.17. Diagram showing the CMC for SDS/n-octanol mixtures (taken from ref. 67) and the CAC for PEO/SDS/n-octanol mixtures for 15 ppm PEO ($M_w = 8 \times 10^6$) in jets 2 (71) and 500 ppm PEO ($M_w = 4 \times 10^6$) in jets 1 (this work).]
3.4. Concluding Remarks

The addition of ethanol to aqueous PEO solutions beyond a certain PEO concentration increases the degree of extension thickening due to promotion of transient entanglement formation as the solvent becomes poorer.

On the other hand, addition of ethanol to PEO/SDS solutions weakens the extension thickening effect induced by SDS beyond the CAC, due to an inhibitory effect of ethanol on the formation of micellar aggregates.

At low contents of alcohol, only long-chain alcohols such as n-octanol are able to promote extension thickening in PEO/SDS solutions. The results show that the main effect of n-octanol is the lowering of the CAC of SDS on PEO. The absence of a measurable effect of SDS/n-octanol comicellization on extension thickening indicates that the most important factor determining changes in extension thickening is the number of micellar aggregates attached to each chain rather than their composition.

Finally, from an application point of view, the results have shown that relatively small amounts of a long chain alcohol can promote aggregation of SDS along the polymer chain, thus enhancing PEO intermolecular network formation in elongational flows.
CHAPTER IV

ELONGATIONAL FLOW OF SOLUTIONS OF POLY(ETHYLENE OXIDE) AND SULFONATED SURFACTANTS

4.1 Introduction

The interactions between certain mixtures of polymers and surfactants have been a subject of interest for many years. Particularly, the interactions between poly(ethylene oxide) (PEO) and sodium dodecyl sulfate (SDS) in aqueous solutions have been extensively explored. Such interactions consist on the formation of surfactant micellar aggregates that attach along the PEO chain. These aggregates form at SDS concentrations that are higher than the critical aggregation concentration (CAC), reported to be in the range 4.1-5.4 mM at 20°C, which is substantially lower than the critical micellar concentration (CMC) of the surfactant (8.3 mM at 20°C). This aggregation process is known to influence the rheological behavior of the solutions as well as their physicochemical properties (3).

Several studies have focused on the determination of the viscosity of PEO/SDS solutions using shear rheometry (38,42,44,45,50,52). The results show that the presence of micellar aggregates along the polymer chains leads to an increase in shear viscosity. This mainly is a consequence of PEO coil expansion due to electrostatic repulsion between the negatively-charged micellar aggregates attached to the PEO chain. The viscosity increases as the SDS concentration is increased from the CAC until it reaches a maximum value that corresponds to saturation of the polymer molecules with micellar
aggregates (38). This concentration is called the polymer saturation point (PSP).

Figure 4.1. Pressure drop in opposed jets (internal diameter: 0.55 mm, jets separation: 1.2 mm) as a function of strain rate for PEO solutions ($M_w = 4 \times 10^6$). Values in the legend represent PEO concentrations (58).

In a previous work (58), we have investigated the elongational flow behavior of PEO/SDS solutions. Semi-dilute solutions of flexible polymers such as PEO exhibit extension thickening in flow fields with appreciable elongational components, as opposed to their shear-thinning behavior in flows where shear components predominate. Flows with important elongational components are encountered in practice in flows through contractions and expansions, and in flow through porous media (12). A nearly ideal elongational flow that resembles uniaxial extension can be created in an opposed-jets device. This system has been widely used in the study of elongational flow of polymer
solutions (16,21). To illustrate the behavior of flexible polymers in opposed jets, Fig. 4.1 shows curves of pressure drop vs. strain rate for flow of aqueous solutions of a high molecular weight PEO as a function of polymer concentration. An important characteristic of this flow is that isolated polymer molecules in a fluid element that passes close to the stagnation point, thus providing enough residence time, undergo a coil-stretch transition when subjected to a high enough strain rate. Experimentally, the coil-stretch transition can be detected by visualization of birefringence patterns when a laser beam is passed through a region around the stagnation point, located between crossed polarizers. The birefringence patterns observed for the 1000 ppm PEO curve in Fig. 4.1 are shown in Fig. 4.2. At low strain rates, the flexible PEO molecules are in a coiled state and no birefringence is observed, since the solution is optically isotropic. As the strain rate increases, the polymer undergoes a coil-stretch transition evidenced by a bright and narrow birefringent line around the stagnation point. This occurs even in semi-dilute solutions, since at low strain rates the molecules are able to disentangle from one another and stretched as if in isolation (16,21). Since coil stretching occurs only in a region close to the line of symmetry, the pressure drops do not increase appreciably with respect to water. Further increases of the strain rate lead to a thickening of the birefringent line, which darkens in the center forming what is termed a “pipe” pattern. In this regime, the increase in the elongational viscosity of the solution around the axis of symmetry causes a change in the flow field that allows the molecules to relax back to the coil state. As the strain rate is increased even further, the flow becomes unstable and the birefringence patterns become delocalized and unsteady. At this point, a clear extension thickening
effect is observed in the pressure drop curves, which is the product of the formation of transient entanglements of polymer molecules, a trademark of semi-dilute solution behavior for flexible polymers in opposed jets flow (16). This is the so-called "flare" regime due to the brightness and unsteady nature of the birefringence patterns.

![Graph showing the relationship between pressure drop (ΔP in kPa) and strain rate (\(\dot{\varepsilon} \text{ s}^{-1}\)). The graph includes points labeled 1. Coil, 2. Stretch, 3. Pipe, and 4. Flare.](image)

Figure 4.2. Pressure drop and birefringence patterns for the 1000 ppm PEO solution (\(\bar{M}_w = 4 \times 10^6\)) in Fig. 4.1. The solid line corresponds to water. The insets show photographs of the region between the opposed capillaries, which are located between crossed polars. The capillaries are aligned horizontally.

The presence of micellar aggregates of SDS attached to the polymer chains and the subsequent changes in polymer conformation have a dramatic effect on the extension thickening of PEO solutions, as revealed by our previous work on porous media flows (53) and flow in opposed jets (58). Figure 4.3 shows pressure drops across the opposed jets vs. strain rate for a fixed PEO concentration as the SDS concentration is increased.
The presence of surfactant starts influencing the pressure drops at concentrations between 5.0 and 5.4 mM, indicating a range where the CAC is located. The onset strain rate for the formation of transient entanglements is decreased by more than an order of magnitude before saturation of the PEO chains with micellar aggregates is achieved. This result indicates that micellar aggregates induce an increase in the interactions between polymer molecules. Three effects might be responsible for such increase: the coil expansion produced by the electrostatic repulsion between aggregates, the increase in the effective volume of the chain by the attached aggregates, and intermolecular interactions between two or more PEO chains that may be attached to the same aggregate (i.e., bridging of PEO chains through SDS micelles).

![Figure 4.3. Pressure drop in opposed jets for PEO/SDS solutions at [PEO]=500 ppm. The polymer and experimental system are those specified in Fig.4.1. Values in the legend represent SDS concentrations (58).](image)
Interactions between PEO and other types of anionic surfactants have been reported, although to a much lower extent than for the PEO/SDS system. The effect of alkyl chain length for alkyl sulfate surfactants has been studied. Several works (72-75) have shown that the CAC of the surfactant decreases with increasing chain length of the alkyl sulfate. Sulfonates have received considerable attention due to their importance in tertiary oil recovery (76) and in other applications such as laundry products, dishwasher liquids and personal care products (77-79). Examples of commonly used sulfonates are sodium dodecyl benzene sulfonate (SDBS) and α-olefin sulfonates (AOS).

Surface tension and conductivity measurements have shown that the CMC of SDBS in aqueous solution is 2.0 mM at 35°C (78). With surface tension and dye solubilization, the reported value of the CMC at 25°C is between 1.1 and 1.2 mM (1,80,81). Also reported in the literature are properties of free micelles such as the aggregation number, corresponding to a value of 75, as determined by steady state fluorescence quenching of a solution containing 5 mM SDBS (78).

Interactions of SDBS with nonionic polymers in aqueous solution have been studied for PEO of $M_w = 200,000$ (81), and poly(vinyl pyrrolidone) (PVP) of $M_w = 40,000$ (82). Surface tension measurements with PEO/SDBS solutions (81) showed trends similar to the PEO/SDS system, with two clear behavioral transitions at the CAC and PSP. For a PEO concentration of 0.2%, a binding ratio at the PSP of 0.038 mol SDBS per mol of ethylene oxide unit was determined (81). This is significantly lower than that for the PEO/SDS system, reported to be 0.2-0.3 mol SDS per mol of ethylene oxide unit (31,32,83,84). Results of dye solubilization in a 0.2% PEO solution indicate that the CAC
of SDBS is 0.6 mM, and the PSP is 2.1 mM, which is consistent with the surface tension results. Electron spin resonance experiments showed that the nature of the interactions between PEO and SDBS is similar to that between PEO and SDS in that it is characterized by partial penetration of the PEO molecules in the outer surface of the aggregate (81). Very similar trends to those observed with SDBS have resulted from studies of the interactions between a PEO with $M_w = 20,000$ and sodium dodecyl sulfonate (85).

The interactions of SDBS with PVP were studied using equilibrium dialysis, surface tension, viscosity, ultrasound velocity, and ultrasound absorption techniques (82). These results also were consistent with an aggregation process similar to that observed in the PEO/SDS system.

Information about the micellar properties of $\alpha$-olefin sulfonates (AOS) in aqueous solutions is not abundant, since most of the work on AOS has been patented (79). The literature mostly deals with synthesis mechanisms, and the usefulness of AOS in laundry products, dishwasher liquids and personal care products (77). Commercial AOS consists of mixtures of compounds, prepared from linear $\alpha$-olefins ($CH_3(CH_2)_nCH=CH_2$). The two main $\alpha$-olefin fractions used as starting material are $n=9$ to $13$ and $n=13$ to $15$ (1).

Surface tension experiments yielded a value for the CMC of about 1.6 mM for an AOS with mostly fractions of $C_{16}$ and $C_{18}$ (86). Other studies with an AOS containing almost equal amounts of $C_{14}$, $C_{16}$ and $C_{18}$ revealed a CMC of 4.2 mM (79). The composition of the AOS used by the different research groups appears to be the cause of the differences in the results. We are not aware of information in the literature regarding
interactions of AOS with any polymer.

In this work, we use the opposed jets system to study how polymer/surfactant interactions in the systems PEO/SDBS and PEO/AOS affect the rheological behavior of solutions of high-molecular weight PEO in elongational flows. These experiments also will allow for comparisons with the behavior of PEO/SDS solutions in elongational flow, and will help in finding more evidence about the mechanisms of interaction between PEO and anionic surfactants containing sulfonates as hydrophilic groups.

4.2 Experimental

A diagram of the experimental set up is shown in Fig. 4.4. The apparatus is the same used in previous investigations (58,87). Two different sets of opposed capillaries were used. The capillaries in one set (jets 1) have an internal diameter \( D = 0.55 \) mm, and a separation \( \delta = 1.2 \) mm. The capillaries in the second set (jets 2) have \( D = 0.60 \) mm, and \( \delta = 1.2 \) mm. The two sets yield somewhat different pressure drops for pure water, but the capillary size does not appreciably affect the results presented in this work. Both sets of jets are located at the center of test cells with dimensions 2.5 cm x 2.5 cm x 10 cm, ensuring that the liquid is stagnant away from the region between the jets. The flow is induced by a vacuum pump that sucks the fluid from the feed reservoir, through the opposed jets, and into a receiving reservoir. The measurement of the fluid flow rate is done by monitoring the pressure drop (measured by a pressure transducer) through a capillary tube \( (\Delta P_1) \) with internal diameter lower than 0.44 mm and length 7 cm that lets air into the feed reservoir at a volumetric rate equal to the flow rate of liquid \( (Q) \) that goes into the test cell. The pressure drop through the jets \( (\Delta P_2) \) is recorded between a point in
the test cell where the liquid velocity is negligible and the exit, by a second pressure
transducer. The average strain rate in the extensional flow field is calculated by

\[ \dot{\varepsilon} = \frac{4Q}{\pi D^2 b} \]  

(4-1)

A control program in the PC manipulates the solenoid valve to set the desired value
of strain rate. A steady state point is recorded once the measurements have stabilized. All
the experiments consist of a controlled increase of strain rate starting from rest. Previous
work (58) has shown that depending on how the flow is set, pressure drop vs. strain rate
curves might exhibit hysteresis.

The birefringence around the stagnation point is visualized by an optical train
consisting of a 10 mW He-Ne laser, crossed polarizers and a λ/4 plate. A microscope at
the end of the optical train is used to visualize the birefringence patterns.

All the experiments were conducted at 20°C. In the experiments, we measure the
pressure drop and observe the birefringent patterns as a function of strain rate, varying
the polymer and surfactant concentrations. Three different PEOs were used; they were
polydisperse samples: one was provided by Polysciences with \( M_w = 8 \times 10^6 \) and the other
two were provided by Polysciences and by Scientific Polymer Products, both with
\( M_w = 4 \times 10^6 \). Both of the samples provided by Polysciences were used in mixtures with
80% pure SDBS obtained from Sigma-Aldrich. The chemical structure of SDBS is given
in Fig. 4.5:

\[
\begin{align*}
\text{O} & \quad \text{Na}^- \\
\text{O} & \quad \text{S} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

Figure 4.5. Chemical structure of SDBS.

The sample provided by Scientific Polymer Products was used in mixtures with AOS
obtained from Albright & Wilson. Mass spectrometry was used to determine the structure
of the AOS. The results show that it consists of 96% of:

\[
\begin{align*}
\text{O} & \quad \text{S} \\
\text{O} & \quad \text{Na}^- \\
\end{align*}
\]

Figure 4.6. Chemical structure of AOS.
The preparation of the solutions consisted on adding the surfactant to water. The polymer is added after the surfactant has been dissolved. The solution was stirred slowly for at least 18 h to ensure total polymer dissolution. The experiments were performed 24 h after preparing the solutions. For solutions containing NaCl, the only difference is that the surfactant and the polymer were added after dissolving the NaCl.

4.3 Results and Discussion

4.3.1 PEO/SDBS Solutions

The effect of addition of SDBS at relatively low concentrations to solutions of a fixed PEO concentration is shown in Fig. 4.7. For the solution without surfactant, this particular PEO concentration yields a pronounced extension thickening effect that sets in at a strain rate \( \dot{\varepsilon}_x = 800 \, \text{s}^{-1} \). As the surfactant concentration is increased, the onset of extension thickening is clearly displaced to higher values of strain rate. This displacement continues until at concentrations between 0.10 and 1.0 mM, there is no evidence of extension thickening in the range of strain rates analyzed, since the curves coincide with that of water. Note that this range of concentration is mostly below the reported CAC for the PEO/SDBS system (0.6 mM). These results suggest that the SDBS is promoting a contraction of the polymer coil. This effect occurs continuously as SDBS is added to the polymer solution, as suggested by the smooth change of \( \dot{\varepsilon}_x \) with SDBS concentration (inset, Fig. 4.7). The absence of a precise onset point for this effect, in terms of SDBS concentration, suggests that it is not a result of the presence of micellar aggregates. In a previous work (58) we have reported increases of \( \dot{\varepsilon}_x \) with surfactant concentration for the PEO/SDS system in 0.1 M NaCl solutions. Intramolecular effects in that case were
explained in terms of interactions of a micellar aggregate with two different segments of the polymer coil, thereby causing coil contraction. However, these effects were observed at SDS concentrations higher than the CAC. The coil contraction in the PEO/SDBS system seems to be a result of changes in the intra-coil environment brought about by the presence of dissolved surfactant molecules.

Figure 4.7. Pressure drop in jets 2 as a function of strain rate for PEO/SDBS solutions at [PEO]=50 ppm ($M_w =8x10^5$). Values in the legend represent SDBS concentrations. Only low SDBS concentrations are shown. The inset shows the onset strain rate for extension thickening ($\dot{e}_o$) as a function of SDBS concentration for these data (88).

Intramolecular effects were not observed in experiments with the PEO/SDS system in the absence of salt, using the same polymer (results not reported) nor for a PEO of lower molecular weight (58). For any PEO molecular weight, the trends were always similar to those observed in Fig. 4.3. The difference between SDS and SDBS might be a
result of the higher hydrophobicity of the SDBS molecule, as reflected by its lower values for the CMC and CAC, which induces increased interactions of free SDBS molecules with the PEO coil.

Figure 4.8. Pressure drop in jets 2 as a function of strain rate for PEO/SDBS solutions at [PEO]=50 ppm ($\bar{M}_w=8\times10^5$). Values in the legend represent SDBS concentrations. Only high SDBS concentrations are shown (88).

The effect of further increases of the SDBS concentration is shown in Fig. 4.8. These results show opposite trends to those in Fig. 4.7: as the concentration of SDBS is increased beyond 1.0 mM, a sizable extension thickening behavior is observed, up to a point at which (at 4.7 mM SDBS) the effect saturates on the pressure drop curves. In this case, as more SDBS is present in solution, there is a decrease in $\dot{e}_s$, which is equivalent to an increase in the disentanglement time of the polymer molecules. This increase in the
disentanglement time is caused by intermolecular interactions, which result from the presence of micellar aggregates along the polymer chains. Three mechanisms are thought to be responsible for this (58): first, electrostatic repulsion between the negatively-charged micellar aggregates along the polymer chain causes coil expansion; second, coil expansion and therefore chain overlap occur due to an increase in the effective volume of the chains; and third, a micellar aggregate can interact with portions of different chains, thus promoting inter-chain contacts.

An interesting aspect of the results shown in Figs. 4.7 and 4.8 is the difference in the criticality of the extension thickening when intramolecular or intermolecular interactions are present. The onset of extension thickening is more abrupt when intramolecular effects are present. For instance, consider the results for 0.03 mM SDBS (Fig. 4.7) and 2.0 mM SDBS (Fig. 4.8). Both solutions have approximately the same \( \dot{\varepsilon}_n \); however, the increase of the pressure drop after \( \dot{\varepsilon}_n \) is more gradual for the 2.0 mM solution. This clearly indicates that the transient entanglements formed in both solutions, even though they have the same relaxation time, are of a completely different nature. This is not surprising since the macromolecules in the two solutions have significantly different structure. For the 2.0 mM SDBS solution, if we take a value of 1.0 mM for the CAC, assume that all the surfactant present beyond the CAC binds to the polymer, and that the aggregation number of the micelles attached to the PEO chain is 75 (which corresponds to free SDBS micelles), we calculate that there are 2000 micellar aggregates per polymer chain. This number seems large, but it corresponds to about 90 EO units per micellar aggregate in the chain. Clearly, a partly expanded coil with 2000 micellar aggregates attached to it (2.0
mM SDBS solution) will exhibit different intermolecular forces than a partly contracted PEO coil without micellar aggregates (0.03 mM solution).

The results presented above show that the effect of SDBS on the elongational flow of PEO solutions is significantly different from the effect of SDS. However, it is interesting to note that, once the polymer saturates with micellar aggregates, both surfactants have very similar effects. Figure 4.9 shows results for PEO/SDS and PEO/SDBS systems at surfactant concentrations higher than the PSP. Both systems have similar pressure drops. This result could indicate that the structure and distribution of micellar aggregates is similar for both surfactants once the chain is saturated. Similar results were obtained at other PEO concentrations (not shown).

![Figure 4.9](image)

*Figure 4.9. Comparison between saturated PEO/SDS and PEO/SDBS solutions (both at 10.3 mM surfactant concentration) in jets 2 at [PEO]=25 ppm (Mw =8x10^5). The PEO solution and water results are shown for comparison (88).*
Figure 4.10 shows the effect of SDBS on solutions with 25 ppm PEO. Strong intramolecular effects are also observed. However, due to the lower polymer concentration (compared to Figs. 4.7 and 4.8), less SDBS is needed for the solutions to completely suppress extension thickening in the range of strain rates explored. The results also show that a higher SDBS concentration is required to induce extension thickening again: note that 3.0 mM SDBS is very similar to water for 25 ppm PEO (Fig. 4.10), whereas the same SDBS concentration leads to a strong extension thickening effect for 50 ppm (Fig. 4.8). This might be a consequence of the fact that more micellar aggregates are needed to re-establish extension thickening after the coil has contracted.
due to the lower polymer concentration. In addition the 25 ppm PEO solution needs a higher concentration of surfactant to achieve its maximum degree of extension thickening. This might be a consequence, not of an increase of the PSP at lower PEO concentration, but of the decreased sensitivity of the extension thickening effect to the presence of micellar aggregates.

Figure 4.11. Pressure drop in jets 2 as a function of strain rate for PEO/SDBS solutions at [SDBS]=1.0 mM at different PEO concentrations \( \langle M_w \rangle =8\times10^6 \). Values in the legend represent SDBS concentrations. (a) 50 ppm PEO. (b) 100 ppm PEO. (c) 200 ppm PEO. (d) 300 ppm PEO (88).

Figure 4.11 shows results for a fixed SDBS concentration (1.0 mM) at several
concentrations of PEO. For the lower PEO concentrations (50 and 100 ppm), pressure drops are clearly lower when SDBS is present, whereas for 200 and 300 ppm, the pressure drop values for the solutions with and without surfactant are almost indistinguishable. Intramolecular effects are important only for solutions that can be "transformed" into dilute solutions when the coils contract. This occurs only when the PEO concentration is low enough so that the density of chain overlap is very low or nonexistent at low strain rates. However, for higher concentrations (Fig. 4.11d), the large degree of coil overlap prevents effects of coil contraction on the extension thickening.

In the polymer concentration regime employed in this work, extension thickening should be observed only for polymers with a sufficiently high molecular weight and hence, we expected intramolecular effects to become less important for lower PEO molecular weights. To explore this, we have employed a PEO with a substantially lower average molecular weight, $\bar{M}_w = 4 \times 10^6$. For this case, Fig. 4.12 shows pressure drop curves for PEO/SDBS solutions at a fixed PEO concentration (500 ppm). The trends observed upon addition of SDBS are very similar to those observed for the PEO/SDS system (Fig. 4.3), where there was no evidence of intramolecular interactions. At SDBS concentrations of 1.0 mM or below, there is no appreciable difference from the pure PEO solution, whereas for higher concentrations, the result is an increase of the disentanglement time (decrease in $\dot{\varepsilon}_n$) of the molecules due to enhanced intermolecular interactions. The effect on extension thickening appears to saturate when the SDBS concentration is 6.0 mM. Further addition of SDBS resulted in no change with respect to the solution with 6.0 mM (results not shown).
Figure 4.12. Pressure drop in jets 2 as a function of strain rate for PEO/SDBS solutions at [PEO]=500 ppm (\(\bar{M}_w=4\times10^6\)). Values in the legend represent SDBS concentrations (89).

Results with 250 ppm PEO and \(\bar{M}_w=4\times10^6\) are shown in Fig. 4.13. Notice that in this case, the pure polymer solution does not exhibit extension thickening. The CAC observed in this case would appear to be between 1.0 and 1.5 mM, and the maximum pressure drops are observed when the SDBS concentration is approximately 5.0 mM. However, at SDBS concentrations beyond 5.0 mM, the solutions start showing progressively lower pressure drops for each strain rate value, as well as higher \(\dot{\varepsilon}\). This could be explained in terms of a decrease in the strength of the repulsion between the micellar aggregates due to screening of their charges by the larger amount of sodium ions in solution at higher surfactant concentrations. The consequence of this is a reduction in
the degree of coil expansion. This is similar to the decrease in shear viscosity observed for PEO/SDS at surfactant concentrations higher than the PSP (38).

![Graph showing pressure drop in jets as a function of strain rate for PEO/SDBS solutions at [PEO]=250 ppm (\(\bar{M}_W = 4 \times 10^6\)). Values in the legend represent SDBS concentrations (89).](image)

The effect of surfactant addition on \(\dot{\varepsilon}_n\) for PEO solutions (\(\bar{M}_W = 4 \times 10^6\)) is presented in Fig. 4.14 as a function of PEO concentration for pure polymer solutions, and for solutions with 2.0 and 7.0 mM SDBS. Note that \(\dot{\varepsilon}_n\) is reduced by an order of magnitude for the 7.0 mM SDBS solutions when compared to pure PEO solutions at low PEO concentrations. For PEO concentrations below 750 ppm and 7.0 mM SDBS, the polymer chains are already saturated with micellar aggregates, and the decrease in \(\dot{\varepsilon}_n\) with PEO concentration is abrupt. On the other hand, although the 2.0 mM SDBS/PEO solutions exhibit lower \(\dot{\varepsilon}_n\) values than the pure polymer solution, there is no appreciable change
with PEO concentration. These solutions never saturate with micellar aggregates, and as the PEO concentration increases, there is a lower number of micellar aggregates per polymer chain. For this reason, the $\dot{\varepsilon}_n$ values tend to get closer to those for pure PEO.

![Figure 4.14. Onset strain rate required for extension thickening in jets 2 for PEO ($M_w = 4 \times 10^6$) and PEO/SDBS solutions as a function of PEO concentration. Values in the legend represent SDBS concentrations (89).](image)

As the results in Fig. 4.14 show, the onset of entanglements is very sensitive to PEO concentration, and it diverges to infinity at a low but finite PEO concentration. This limiting concentration corresponds to the minimum concentration for coil-coil interactions in the flow ($c^-$). Its value can be determined by plotting the disentanglement time, $\lambda_e = 1/\dot{\varepsilon}_n$ vs. [PEO], and extrapolating the concentration to $\lambda_e = 0$. For the PEO solutions this value is $c^- \approx 170$ ppm. Notice that $c^-$ is substantially lower than the coil overlap concentration under static conditions, which in this case is $c^* \approx 800$ ppm, due to
the PEO conformational changes induced by the extensional flow field. The value of $c^*$ for the PEO/SDBS solutions with 7.0 mM SDBS is below 1 ppm. This represents a reduction of two orders of magnitude in the PEO concentration that represents the limit between the dilute and the semi-dilute regimes in extensional flow.

The previous results indicate that an enhancement in the extension thickening behavior of the PEO solutions can be obtained by addition of SDBS. Figure 4.15 illustrates the dramatic increase in extension thickening induced by SDBS by comparing solutions of pure PEO of a sample with $\overline{M}_w = 4 \times 10^6$ (Fig. 4.15a) with solutions of the same polymer at a fixed SDBS concentration (4.5 mM). Notice that at a PEO concentration of 250 ppm, the behavior of the pure PEO solution is close to that of water,

Figure 4.15. Pressure drop in jets 2 as a function of strain rate for (a) PEO solutions, and (b) PEO/SDBS solutions with [SDBS]=4.5 mM at different PEO concentrations ($\overline{M}_w = 4 \times 10^6$). Values in the legend represent PEO concentrations (89).
since the solution is nearly dilute. In the presence of SDBS, however, the solution exhibits pressure drops that are even higher than those for PEO solutions with over 1000 ppm.

![Pressure drop in jets as a function of strain rate for PEO/SDBS solutions at [PEO]=25 ppm (MW=8x10^6) in 0.1 M NaCl. Values in the legend represent SDBS concentrations (88).

4.3.2 PEO/SDBS in NaCl solutions

The effect of electrolytes in solution was also studied. In the presence of 0.1 M NaCl, PEO/SDBS solutions with PEO of MW=8x10^6 exhibit similar behavior as in the absence of salt. This is illustrated by Fig. 4.16. The range of concentrations in which intermolecular effects start to appear seems to be the same as without salt (compare with Fig. 4.10), although saturation of the enhancement of extension thickening seems to
occur at a lower SDBS concentration (4.7 mM) in the presence of salt. Therefore, the presence of salt still has an effect on the aggregation. This is better illustrated by the results in Fig. 4.17, where the effect of PEO concentration is compared for solutions with and without salt for a fixed SDBS concentration (8.2 mM) and various polymer concentrations. Extension thickening is only observed for PEO concentrations above 7.5 ppm in the presence of NaCl. At lower PEO concentrations, the electrostatic screening by sodium ions allows for contraction of the coils to a degree such that extension thickening is suppressed. However, once intermolecular interactions are present at higher PEO concentrations (e.g. 25 ppm), the rate of increase in pressure drop is higher in the presence of NaCl. This behavior is similar to what is observed for PEO/SDS solutions in the presence of salt (58).

\[
\begin{align*}
\Delta P \text{ (kPa)} & \\
0 \text{ M NaCl} & \\
0.1 \text{ M NaCl} & \\
\end{align*}
\]

Figure 4.17. Pressure drop in jets 2 as a function of strain rate for PEO/SDBS solutions at [SDBS]=8.2 mM at different PEO concentrations (\(M_w=8\times10^5\)) (a) without salt, and (b) in 0.1 M NaCl. Values in the legend represent PEO concentrations (88).
We also have explored the effect of polymer concentration for a fixed SDBS concentration (11.0 mM) in the presence of NaCl for the PEO with $M_w=4\times10^6$. The pressure drop results are presented in Fig. 4.18. The strain rate $\dot{\varepsilon}_e$ decreases as the PEO concentration increases from 250 to 750 ppm and the extension thickening effect becomes more pronounced. In this case, the transition to entanglements (flare regime) occurs rather abruptly with a discontinuity in the pressure drop curves. When the PEO concentration reaches 1000 and 1250 ppm, even though the rate of increase of pressure drop increases with polymer concentration, as expected, the value of $\dot{\varepsilon}_e$ increases to a point that, for instance, at strain rates close to 4000 s$^{-1}$, the 250 ppm PEO solution exhibits higher pressure drops than the 1250 ppm solution. This effect coincides with a change in shape of the pressure drop curves that acquire a more pronounced downward curvature as the PEO concentration is increased. This same shape difference was observed for the first time in PEO/SDS solutions with NaCl (58). The curves exhibit higher pressure drops at low strain rates followed by a region where the rate of increase in pressure drop decreases. In this region, instabilities in birefringence pattern are observed in the region between the capillaries, unlike the flare pattern, which is observed in regions relatively far from the stagnation point. This pattern might be caused by the large increase of extensional viscosity of the solution around the stagnation point, brought about by deformed PEO coils with relatively large attached micellar aggregates. The extension thickening produced by these flow instabilities decreases in strength at higher strain rates, which might be a consequence of the reduction in the residence time.
of the molecules in the flow field.

![Graph showing pressure drop (ΔP) as a function of strain rate (d) for PEO/SDBS solutions at SDBS=1.10 mM (MW=4x10^6) in 0.1 M NaCl. Legend values represent PEO concentrations in ppm.]

Figure 4.18. Pressure drop in jets 2 as a function of strain rate for PEO/SDBS solutions at [SDBS]=1.10 mM (MW=4x10^6) in 0.1 M NaCl. Values in the legend represent PEO concentrations (89).

In order to evaluate how the intramolecular effects change with PEO concentration in the presence of NaCl, we present in Fig. 4.19 a plot of $\dot{\varepsilon}$, as a function of SDBS concentration. Intramolecular interactions (as evidenced by increase in $\dot{\varepsilon}$) occur from very low surfactant content. The values of $\dot{\varepsilon}$ continue to increase until a maximum value is reached, and then a decrease is observed due to the formation of intermolecular interactions. The results show different trends at different SDBS concentrations. At SDBS concentrations below 1.5 mM, an increase in polymer concentration leads to a decrease in $\dot{\varepsilon}$, as it happens in the absence of surfactant. However, there is a range of
SDBS concentration (approximately 5.0 to 11.0 mM) in which a higher PEO concentration results in higher values of $\dot{\varepsilon}_n$, indicating that transient entanglement formation weakens.

Figure 4.19. Strain rate required in jets 2 for transient entanglements for PEO ($M_w = 4\times10^6$) and PEO/SDBS solutions in 0.1 M NaCl as a function of SDBS concentration. Values in the legend represent PEO concentrations (89).
4.3.3 PEO/AOS Solutions

Figure 4.20 shows results for a fixed polymer concentration (300 ppm, $\bar{M}_w = 4 \times 10^5$) at several concentrations of AOS. At an AOS concentration of 0.3 mM, the onset for transient entanglements is displaced to higher strain rate values than that for the pure polymer solution, as intramolecular effects contract the PEO coils. Such increase in $\dot{\varepsilon}_n$ goes on as the surfactant concentration increases to 1.0 mM. The behavior is similar to that observed for SDBS/PEO of a higher molecular weight (Fig. 4.7), except that extension thickening is never completely eliminated in the range of strain rates studied. This is most likely due to the higher polymer concentration used. As the AOS concentration is increased beyond 1.0 mM, intermolecular interactions gain importance, and the solution with 2.0 mM AOS displays the lowest $\dot{\varepsilon}_n$. For AOS concentrations greater than 2.0 mM, the pressure drop curves approach the curve of the pure polymer solution. This behavior is similar to that described in Fig. 4.13 for PEO/SDBS, in which the excess of surfactant could be inducing a decrease in the repulsion between micellar aggregates due to the screening of charges by the sodium ions in solution, and the consequent coil contraction. To test this hypothesis, we added 1.0 mM NaCl to the 2.0 mM AOS solution in Fig. 4.20 to see if the pressure drop curve would be displaced to higher strain rates, resembling more the 3.0 mM AOS curve. However, the addition of 1.0 mM NaCl had no effect on the 2.0 mM AOS curve. This does not rule out coil contraction due to electrostatic interactions, since obviously adding 1.0 mM NaCl would not produce the same effect on ionic strength as adding 1.0 mM AOS, but it indicates a more complex pattern of interactions between the polymer and the surfactant in the
presence of salt.

![Pressure drop in jets as a function of strain rate for PEO/AOS solutions at [PEO]=300 ppm (\(M_w = 4 \times 10^6\)). Values in the legend represent AOS concentrations.](image)

Birefringence observations for PEO/AOS solutions are presented in Fig. 4.21. The pipe/flare transition coincides with the onset of extension thickening in the pressure drop curves. This observation was common to all the solutions analyzed in the present work. The initial increase of the strain rate for pipe/flare transition (\(\dot{\varepsilon}_s\)) is a reflection of intramolecular interactions. This effect seems to saturate before intermolecular effects set in at 1.0 mM AOS. No appreciable changes, within the sensitivity of the observation, are observed for the coil/stretch transition strain rate.
As was the case for the PEO/SDBS system (Fig. 4.11), the presence of intramolecular effects depends on polymer concentration. Figure 4.22 shows a comparison of the behavior of solutions with the same AOS concentration and different PEO concentrations. Addition of AOS to the 150 ppm PEO solution clearly causes coil contraction. At 200 ppm PEO, the surfactant has no appreciable effect. At 300 ppm PEO, the surfactant enhances intermolecular interactions, but this effect disappears as the polymer concentration is further increased to 1000 ppm due to a reduction of the number of micellar aggregates per chain.
The presence of NaCl in PEO/SDS solutions exhibits trends similar to PEO/SDBS solutions, but the effect of the presence of AOS is less significant. Figure 4.23 shows the effect of the AOS concentration on solutions with 300 ppm PEO and 0.1 M NaCl. The shape of the curves has changed when compared to solutions in the absence of NaCl, and the birefringence observations also indicate a qualitative difference in the nature of the
flow (compare with Fig. 4.18). In the case of the AOS, however, no intramolecular interactions were observed in the presence of salt.

![Pressure drop in jets 1 as a function of strain rate for PEO/AOS solutions at [PEO]=300 ppm ($\bar{M}_w = 4 \times 10^4$) in 0.1 M NaCl. Values in the legend represent AOS concentrations.](image.png)

**Figure 4.23.** Pressure drop in jets 1 as a function of strain rate for PEO/AOS solutions at [PEO]=300 ppm ($\bar{M}_w = 4 \times 10^4$) in 0.1 M NaCl. Values in the legend represent AOS concentrations.

### 4.4 Concluding Remarks

Molecular interactions between SDBS and the PEO chain affect the extension thickening behavior of the polymer solutions. At low PEO concentrations and for the higher molecular weight PEO, the surfactant induces contraction of the polymer coil and a consequent reduction in extension thickening. The occurrence of these intramolecular interactions shows a strong dependence on PEO concentration and molecular weight. At surfactant concentrations higher than the CAC reported by other methods, intermolecular
interactions are also observed as evidenced by the increase in the apparent elongational viscosity of the solution. These interactions are due to the presence of micellar aggregates along the polymer chain. Interactions between PEO and AOS are of similar character to those between PEO and SDBS, although intramolecular interactions are clearly observed for solutions of the lower molecular weight PEO.
CHAPTER V

TRANSIENT BEHAVIOR IN SOLUTIONS OF POLY(ETHYLENE OXIDE) AND SULFONATED SURFACTANTS

5.1. Introduction

It is well known that polymers in aqueous solutions undergo thermally induced scission as time passes by. This is a form of polymer degradation. As a consequence, a fluid that originally exhibits a high apparent viscosity due to the friction between large molecules and water exhibits a decrease in viscosity with time as the molecules break. For this reason, in applications where a fluid with specific rheological characteristics is required, it is important to characterize any changes of the fluid properties with time.

In the case of solutions involving a polymer and a surfactant, it is interesting to determine whether the complexes that form undergo changes with time, such as structure rearrangements that induce a change in the macroscopic behavior of the solution.

In this work, the opposed-jets device is used to study the transient behavior of the systems studied in the preceding chapters, namely: PEO/SDS, PEO/SDBS and PEO/AOS.

5.2. Experimental

The experimental set up is the same shown in Figs. 2.2, 3.4 and 4.4. The experiments were performed in two different sets of capillaries. The first set (jets 1) consists of capillaries with an internal diameter $D=0.55$ mm and a separation $\delta=1.2$ mm; the second set of capillaries (jets 2) have $D=0.60$ mm and $\delta=1.2$ mm.
All of the experiments were conducted at 20°C. In the experiments, we measure the pressure drop and observe the birefringent patterns as a function of strain rate, varying the polymer and surfactant concentrations. Two different PEOs were used; they were polydisperse samples. One was provided by Polysciences with $M_w = 8 \times 10^6$, and the other was provided by Scientific Polymer Products with $M_w = 4 \times 10^6$. The sample provided by Polysciences was used in mixtures with 80% pure SDBS obtained from Sigma-Aldrich. The sample provided by Scientific Polymer Products was used in mixtures with 99% pure SDS from Sigma-Aldrich and with AOS obtained from Albright & Wilson (see Chapter IV for details).

The solutions were prepared in a beaker previously washed with deionized water. The total volume of solutions prepared was 4000 ml. The beaker was filled with 2000 ml of deionized water. The water was stirred at approximately 900 rpm in order to obtain a deep vortex. Once the vortex was stable, the surfactant was added to the water, and after total surfactant dissolution, the polymer was slowly added on the vortex walls to ensure the polymer was dispersed completely. After all the polymer was added, the stirring velocity was decreased to 75 rpm, and 2000 ml of deionized water were added to the beaker to complete the 4000 ml. The solution was stirred slowly, controlling the stirring speed at 75 rpm for at least 18 h to ensure total polymer dissolution. The slow stirring is fundamental for the preparation of the solutions, since PEO in water is very susceptible to mechanical degradation (12).

For solutions containing NaCl or ethanol, the only difference was that the surfactant and the polymer were added after dissolving the NaCl or ethanol in water. The
experiments were performed at different times, usually not less than 24 h after solution preparation. The procedure is as follows: a batch of solution is prepared, and certain volume of that batch is passed through the opposed jets. Experiments performed at the specified times require the use of fresh solution from the original batch, so the volume that has already been subjected to flow between the opposed jets is discarded. The reason is that the polymer molecules in the solution that has passed through the opposed jets have already suffered flow-induced mechanical degradation (12). The beaker containing the solution is stored at 20°C without further stirring in order to prevent mechanical degradation of the polymer in solution.

Figure 5.1. Pressure drop in jets 1 as a function of strain rate for a PEO solution at [PEO]=300 ppm ($\overline{M}_w = 4 \times 10^5$). Values in the legend represent the time at which the experiment was performed.
5.3. Results and Discussion

Figure 5.1 shows curves of pressure drop vs. strain rate for a solution of 300 ppm PEO ($\overline{M}_w = 4 \times 10^6$) at different times after solution preparation. After 161 h, the pressure drops have barely changed compared to those corresponding to 20 h after preparation. The value of $\dot{\varepsilon}_n$ has increased about 200 s$^{-1}$, which does not represent an appreciable change. This shows that within this time period, any thermal degradation of the PEO does not have an impact on its behavior in opposed jets flow. A similar experiment was done on a solution of 300 ppm PEO ($\overline{M}_w = 4 \times 10^6$) in the presence of 6.0 mM SDS. Figure 5.2 shows that 73 h after the solution was prepared, the pressure drops have not changed. Once again, these solutions are stable with time.

![Figure 5.2. Pressure drop in jets 1 as a function of strain rate for a PEO/SDS solution at $[\text{PEO}]=300$ ppm ($\overline{M}_w = 4 \times 10^6$) and $[\text{SDS}]=6.0$ mM. Values in the legend represent the time at which the experiment was performed.](image)
The behavior of PEO/SDBS solutions is different from pure PEO and PEO/SDS solutions. Figure 5.3 shows the results for a solution of 50 ppm PEO ($\overline{M}_w=8\times10^6$) and 9.4 mM SDBS. The curve corresponding to 24 h after the solution was prepared shows that this amount of SDBS promotes strong intermolecular interactions between the polymer molecules. The value of $\dot{\epsilon}_a$ is considerably lower than that for the pure polymer solution. After 53 h, however, the pressure drops are very close to those of water, and formation of transient networks has been entirely suppressed. As shown in Figs. 5.1 and 5.2, 53 h represents a period of time where the behavior of the PEO and PEO/SDS solutions does not change. This result suggests a particular characteristic of the
PEO/SDBS systems. The effect of time has also been investigated for the PEO/AOS system.

![Graph showing pressure drop curves](image)

Figure 5.4. Pressure drop in jets as a function of strain rate for a PEO/AOS solution at $[\text{PEO}]=300$ ppm ($\overline{M}_w=4\times10^6$) and $[\text{AOS}]=2.0$ mM. Values in the legend represent the time at which the experiment was performed.

Figure 5.4 shows pressure drop curves for a solution of 300 ppm PEO and 2.0 mM AOS. This amount of AOS promotes intermolecular interactions, due to the lower $\dot{\varepsilon}_n$ when compared to the pure polymer solution. However, as time passes by, $\dot{\varepsilon}_n$ increases, to the point where after 88 h, the pressure drops are almost indistinguishable from those of pure water, although birefringence observations indicated the presence of a thin birefringent line at strain rate values up to 1100 s$^{-1}$. Then, a thin pipe was formed, and no further changes were observed as the strain rate increased. These results suggest that the
differences observed for the solutions containing SDBS or AOS are only induced by their interactions with PEO, since in the period considered, both the behavior of pure PEO and the behavior of PEO/SDS do not change (see Figs. 5.1 and 5.2). Thus, the transient character of PEO/SDBS and PEO/AOS systems constitutes additional experimental evidence of a different type of interactions from those between PEO and SDS.

![Figure 5.5. Pressure drop in jets 1 as a function of strain rate for PEO/AOS solutions at [AOS]=2.0 mM at different PEO concentrations (M_w =4x10^5). PEO concentrations are indicated at the upper corner of the figures. Values in the legend represent the time at which the experiment was performed.](image)

The effect of PEO concentration is shown in Fig. 5.5. In 48 h the solution containing 200 ppm PEO (Fig. 5.5a) shows pressure drops that are equivalent to those of water, whereas the solution containing 1000 ppm PEO (Fig. 5.5b) changes slightly after 267 h. Comparing these results and those shown in Fig. 5.4, it is evident that polymer concentration plays an important role in temporal changes. When the polymer concentration is low, the changes occur faster than at higher polymer concentrations. Intramolecular interactions are less likely to occur at higher polymer concentrations.
since the number of polymer molecules per unit volume is larger and there is a point where the polymer chains are not able to adopt a contracted coil conformation due to the interactions that exist between them even when there is no flow. From this, one may infer that the micellar aggregates induce the formation of intramolecular interactions with time, and higher PEO concentrations introduce a delay in this process.

For the PEO/AOS solutions, it was observed that some particulates were present in the solution after approximately 72 h. These particulates could be PEO and PEO/AOS complexes that precipitated; these were never observed in PEO or PEO/SDS solutions. If PEO precipitated, then the concentration of PEO that remains dissolved is lower, causing the lower pressure drops. For this reason, the precipitate was filtered, and its mass quantified. A solution of 300 ppm PEO and 2.0 mM AOS was filtered after more than 90 h to ensure that it already behaves like water when passed through the opposed jets, and then the filter paper was dried and weighed. The result was that the particulates constituted less than 0.5% of the total mass of PEO and AOS added in the moment of preparation of the solution. The same result was obtained for a solution with 200 ppm PEO and 2.0 mM AOS filtered after more than 50 h. These results suggest that the changes in pressure drop are not due to PEO precipitation, since the amount that apparently precipitated is negligible. This does not preclude, however, the formation of a microphase that coexists with the solution. Nevertheless, turbidity or phase separation were not observed.
In order to obtain more information about the nature of the interactions that lead to transient effects, we wanted to explore whether this transient process is reversible. One way is to change the nature of the solvent by adding ethanol. Previous results by Smitter et al. (87) showed that aqueous solutions of 25% v/v of ethanol difficult the formation of both micelles in solution and micellar aggregates, since this solvent is more hydrophobic than water and a better solvent for the surfactant. Figure 5.6 shows pressure drops for a PEO/SDS solution to which ethanol has been added after 24 h. The pressure drops are the same as those for a PEO solution in 25% v/v ethanol. This indicates that ethanol induced
breaking of the micellar aggregates along the PEO chains, and thus the aggregation process is reversible in PEO/SDS systems. Based on this result, it was thought that if the aggregation process for PEO/AOS systems is also reversible, then adding ethanol to a PEO/AOS solution whose pressure drops are already equivalent to those of water, could induce breaking of the micellar aggregates that promote intramolecular interactions. The result would be pressure drops of the PEO solution in 25% v/v ethanol.

\[ \Delta P \text{ (kPa)} \]

![Graph showing pressure drop (\(\Delta P\) in kPa) as a function of strain rate (\(\dot{\varepsilon}\) in s\(^{-1}\)).](image)

**Figure 5.7.** Pressure drop in jets 1 as a function of strain rate for a PEO/AOS solution at [PEO]=400 ppm (\(\bar{M}_w=4\times10^6\)) and [AOS]=2.7 mM. Ethanol was added after 90 h. Values in the legend represent the time at which the experiment was performed (after dilution with ethanol, the solutions were 25% v/v ethanol with [PEO]=300 ppm and [AOS]=2.0 mM).

Two experiments were done starting from more concentrated solutions of PEO/AOS in water, such that dilution with ethanol resulted in a 25% v/v solution of ethanol with 300 ppm PEO and 2.0 mM AOS. Solutions of 400 ppm PEO and 2.7 mM AOS were
prepared, and after 91 h, both solutions behaved like pure water when passed through the opposed jets. Ethanol was then added at this time to both solutions. Both were passed through the opposed jets at different times. One experiment was done after 1 h and the other one after 94 h, considering two possibilities for a reversible process respectively: (a) instantaneous breaking of micellar aggregates; (b) slow breaking of micellar aggregates. Both solutions did not show a considerable change, but remained close to the behavior of the original solution as seen in Fig. 5.7. However, when ethanol was added at the moment of the preparation of the solution, the resulting curve was indistinguishable from the curve for pure PEO and ethanol, indicating that the addition of AOS did not contribute to the extension thickening of the solution. This solution was also aged for 146 h and there was no change either. These results are shown in Fig. 5.8. It is clear that the interactions between PEO and AOS lead to a suppression of extension thickening with time and are inhibited by the presence of ethanol; but once they occur and extension thickening has been completely suppressed, addition of ethanol has no effect.

We decided to investigate what happens when ethanol is added after PEO/AOS interactions occur, but before extension thickening is suppressed. Figure 5.9 shows that when ethanol is added after 24 h (before the PEO/AOS solution to behaves like water), the pressure drops are very different from those for 300 ppm PEO in 25% v/v ethanol, indicating that even at shorter times the aggregation of AOS is not reversible. However, the solution was passed through the opposed jets after 24 h, and decreased slightly with respect to the solution that was passed through the opposed jets 3 h after addition of ethanol. Also, the pressure drops also increased once the transient networks were formed.
The results indicate that despite the inability of ethanol to completely break the aggregates, it influences the transient process in a way that the approach to the behavior of water is retarded or stopped. Hence, aggregation of AOS and PEO is irreversible once an apparent steady-state of the interactions in solution is reached, and when ethanol is added during the solution preparation this irreversible aggregation mechanism does not occur.

Figure 5.8. Pressure drop in jets 1 as a function of strain rate for PEO solutions at [PEO]=300 ppm (MW =4x10^6). Contents of AOS are 2.0 mM and solutions with ethanol are 25% v/v. Values in parenthesis in the legend represent the times at which the experiments were performed.
Figure 5.9. Pressure drop in jets 1 as a function of strain rate for a PEO/AOS solution at [PEO]=400 ppm (M_w =4x10^6) and [AOS]=2.7 mM. Ethanol was added after 24 h. Values in parenthesis in the legend represent the time at which the experiment was performed (after dilution with ethanol, the solutions were 25% v/v ethanol with [PEO]=300 ppm and [AOS]=2.0 mM).

Transient effects were also explored on solutions with 0.1 M NaCl. Figure 5.10 shows the results for a 300 ppm PEO and 2 mM AOS in the presence of salt. The initial increase in pressure drop does not seem affected by the presence of salt. Birefringent observations show that when this increase occurs, there is a pipe formed in the flow field that is typically thicker than that observed with pure PEO solutions, and it is this extensive flow modification what leads to the increase in pressure drop. As time passes, the main effect is a plateau region extended to higher strain rates, and then an increase in \( \dot{\varepsilon}_n \). The shape of these curves and the time it takes for the changes in \( \dot{\varepsilon}_n \) to occur suggest a mechanism
for the formation of intramolecular interactions that is strongly influenced by the presence of electrolytes in solution.

![Graph showing pressure drop in jets as a function of strain rate](image)

Figure 5.10. Pressure drop in jets 1 as a function of strain rate for a PEO/AOS solution at [PEO]=300 ppm (M_W =4x10^6) and [AOS]=2.0 mM in 0.1 M NaCl. Values in the legend represent the time at which the experiment was performed.

5.4. Concluding Remarks

The solutions containing PEO and SDBS or AOS change their behavior when passed through the opposed jets at different times. Such behavior in polymer solutions is consistent with thermal degradation of the polymer molecules in solution. However, within the period of such changes, experiments show that pure PEO solutions do not undergo any changes in behavior with respect to their behavior after 24 h of preparation.
Similar results were obtained for PEO/SDS systems. For this reason, it is thought that if degradation is the cause of such changes, it should be induced by the presence of the SDBS or AOS.

The results of adding ethanol provide important pieces of information, such as the fact that when added to the solution by the moment of preparation, it inhibits any aggregation of AOS along the PEO chains, and therefore, the behavior of the solution does not change. When ethanol is added after 24 h (after interactions between PEO and AOS occur), the transient process stops. These results suggest that the transient character is due to a reorganization of the micellar aggregates in a way that intramolecular interactions are promoted. The characteristic time of such reorganization is of the order of days, indicating a slow kinetics for this process. However, other researchers (4) have recently reported that addition of Pb^{2+} and S^{2-} to an aqueous solution of PEO/SDS leads to the formation of PbS rodlike structures in a process that takes from 2 to 3 weeks.
CHAPTER VI

STRUCTURAL THEORIES

This chapter consists of an introduction to the use of molecular theories to represent the rheological behavior of polymer solutions and polymer/surfactant solutions. More specifically, aqueous solutions of high molecular weight polymers are considered. Simple models are treated here which try to explain how structural features affect the macroscopic rheology of the bulk fluid. The models studied are based on treating flexible polymer molecules as beads-and-springs, the simplest case being the elastic dumbbell that contains a single spring connecting two beads.

6.1. Polymer Conformation

Since the rheology of a polymer solution is related to the conformation of the polymer molecules dissolved in the solvent, it is important to know what this conformation will be. The backbone of the polymer chain consists of specific covalent bonds, which have lengths and angles formed between adjacent bonds that are restricted to narrow ranges. However, this constraint does not make the chain completely stiff since there are multiple rotational isomers that have the same bond angle in three-dimensional space. According to this, it is evident that polymer molecules are somewhat stiff when observed on a scale of a few bonds. When flexible polymer molecules are dissolved in a solvent at concentrations low enough to consider them as surrounded completely by solvent, their conformation will change with time due to random thermal motion of the atoms of the chain and due to collisions with solvent molecules. The solution is then a dilute solution
since a specific polymer molecule cannot 'see' other polymer molecules. On the average, the shape of the molecule could resemble that of a random coil. A random coil can be generated in the following way: a short straight segment is drawn in a random direction in space; at its end, another segment is drawn in a random direction, and so on. By performing this process with a large number of segments, a structure such as that in Fig. 6.1 is obtained. The length of each segment typically comprises a number of structural units.

![Figure 6.1. Two dimensional representation of a three-dimensional random coil.](image)

Since the conformation of a freely jointed chain is random in nature, its structural characteristics must be represented in terms of statistical variables. Considering a freely jointed chain where one of its ends is located at the origin, the other end can be located with a vector that joins both ends. This vector is denoted as \( \mathbf{R} \) and it is called the 'end-to-end vector' (see Fig. 6.1). Let \( \Psi_0(\mathbf{R}) \) be the equilibrium probability distribution associated with a specific end-to-end vector, meaning that \( \Psi_0(\mathbf{R}) \, d\mathbf{R}^3 \) is the probability that the end-to-end vector lies at a position between \( \mathbf{R} \) and \( \mathbf{R}+d\mathbf{R} \). The freely jointed chain consists of \( N_k \) segments each of length \( b_k \) (90). Using random walk arguments, and
assuming that \( N_k \to \infty \), it can be shown that \( \Psi_o(\mathbf{R}) \) can be approximated to a Gaussian distribution. Such distribution implies that \( \mathbf{R} = 0 \) is the most probable conformation.

An important geometric parameter of the freely jointed chain is the mean square end-to-end distance \( \langle R^2 \rangle_o \) defined as the second moment of the distribution:

\[
\langle R^2 \rangle_o = \int R^2 \Psi_o(\mathbf{R}) d\mathbf{R} = N_k b_k^2
\]

(6-1)

The angular brackets "\( \langle \rangle \)" are used to denote spatial averages weighed by \( \Psi_o(\mathbf{R}) \).

For an arbitrary parameter \( f \), we have:

\[
\langle f \rangle_o = \int f \Psi_o(\mathbf{R}) d\mathbf{R}
\]

(6-2)

The root mean square end-to-end distance \( \sqrt{\langle R^2 \rangle_o} \) is a measure of the size of a polymer molecule in an equilibrium conformation. Another parameter frequently used is the radius of gyration (see Fig. 6.1). The radius of gyration is defined as the root mean square distance separating a structural unit from the center of mass of the molecule. It is related to the root mean square end-to-end distance by:

\[
R_g^2 = \frac{\langle R^2 \rangle_o}{6}
\]

(6-3)

In what follows, \( \langle R^2 \rangle_o \) will also be referred to as \( R_{eq}^2 \).

6.1.1. Mechanical Response of a Random Coil

In order to propose a constitutive equation for a viscoelastic fluid by analyzing what happens at the molecular level, we need to quantify the behavior of the microstructure.
from a mechanical point of view. This means that we want to determine how an applied force on the coil affects the polymer conformation \( \mathbf{R} \). From statistical thermodynamics, it is found that when pulling an end of the chain to produce an end-to-end vector \( \mathbf{R} \), the force to overcome the entropic spring force of the chain is given by (90):

\[
\mathbf{F}^C = \frac{H}{2} \mathbf{R}
\]

(6-4)

where \( H = 2kT\beta^2 \). Here, \( \beta^2 \) is a constant given by:

\[
\beta^2 = \frac{3}{2} \frac{1}{b_k^2 N_k}
\]

(6-5)

Equation 6-4 represents an elastic force: as the chain expands, the force increases proportionally to the end-to-end distance. This is the form of a linear or Hookean spring. Then, the polymer molecule can be seen as an elastic spring whose equilibrium point is \( \mathbf{R}=0 \) (which is also the conformation with the maximum probability). This is an appropriate expression when the molecule is stretched to no more than about a third of its maximum extension (90). Equation 6-4 can also be represented more generally for an arbitrary equilibrium conformation \( \mathbf{R}^* \) instead of \( \mathbf{R}=0 \), becoming:

\[
\mathbf{F}^C = H(\mathbf{R} - \mathbf{R}^*)
\]

(6-6)

The next step is to determine the consequences of this mechanical response in terms of the macroscopic stress tensor.

6.1.2. Polymer Stresses

The stress vector is associated to a specific surface in space. Figure 6.2 represents a
We need to find an expression for the resulting stress on \( dA \) due to the elastic forces given by Eq. 6-4. The total stress will depend on the number of molecules that cross \( dA \). Let \( \nu \) be the number of polymer molecules per unit volume. The molecule is represented by the end-to-end vector \( \mathbf{R} \). For any given \( \mathbf{R} \), the only molecules that can cross the surface \( dA \) are those contained in the volume shown in Fig. 6.2. With these considerations, we find that the total number of molecules with size between \( \mathbf{R} \) and \( \mathbf{R} + d\mathbf{R} \) that cross \( dA \) \((N_i)\) is given by:

\[
N_i = n \cdot \mathbf{R} \, dA \, \nu \, \Psi(\mathbf{R}) \, d\mathbf{R}^3 \tag{6-7}
\]

Multiplying Eq. 6-7 by Eq. 6-4, we obtain an expression for the total force exerted on \( dA \) by the molecules with size between \( \mathbf{R} \) and \( \mathbf{R} + d\mathbf{R} \), and integrating over \( d\mathbf{R}^3 \), the force exerted by all the molecules is obtained. This force per unit area gives the stress vector:
According to the definition given by Eq. 6-2:

\[ \langle \mathbf{R} \mathbf{R} \rangle = \int \mathbf{R} \mathbf{R} \psi (\mathbf{R}) \, d\mathbf{R} \]  

(6-9)

where \( \langle \mathbf{R} \mathbf{R} \rangle \) represents an average value over all possible polymer configurations.

The stress vector is then:

\[ \mathbf{t}_p = 2kT \nu \beta^2 \mathbf{n} \cdot \langle \mathbf{R} \mathbf{R} \rangle \]  

(6-10)

From the definition of stress vector: \( \mathbf{t}_p = \mathbf{n} \cdot \mathbf{\tau}'_p \), and Eq. 6-10, the stress tensor due to the polymer is:

\[ \mathbf{\tau}'_p = 2kT \nu \beta^2 \langle \mathbf{R} \mathbf{R} \rangle \]  

(6-11)

This equation relates what happens at the microscopic level (through \( \langle \mathbf{R} \mathbf{R} \rangle \)) and its consequences on the continuum (through \( \mathbf{\tau}'_p \)). Thus, viscoelastic stresses are produced by distortions of the distribution of polymer configurations.

It is necessary to propose a model to represent the polymer molecules in solution in order to quantify how these deform in a flow field. The simplest one is the elastic dumbbell model.

### 6.2. The Elastic Dumbbell Model. The Langevin's Equation

Flexible polymer molecules are frequently modeled by beads-and-springs chains. The elastic dumbbell model conceptualizes the molecule as being made up of two beads and a
spring connecting them. The spring, when stretched, mimics the elastic forces in flexible polymer molecules, while the beads represent the interaction between the molecule and the solvent. This is a very crude representation of polymer molecules, since it does not account for the details of the molecular architecture. However, the elastic dumbbell is orientable and stretchable, and has played an important role in developing a qualitative understanding of rheological phenomena (91). An elastic dumbbell model is shown in Fig. 6.3.

![Elastic dumbbell with configuration given by vector R. Vector r connects bead 1 and the origin of an arbitrary frame of reference.](image)

A basic force balance will allow us to obtain an equation of motion for the dumbbell such that the changes in $\mathbf{R}$ (end-to-end vector) are related to all possible phenomena that affect the chain conformation. For an elastic dumbbell in a solvent, there are three forces that each bead exerts on its surroundings: the viscous drag exerted by the fluid, the elastic spring force, and random Brownian motion forces due to the impact of the solvent molecules on the beads. Considering both beads to have the same mass, $m$, Newton’s third law of motion for each bead results in:

$$m \frac{d\mathbf{v}_{b1}}{dt} = \mathbf{b}_1 + \mathbf{F}_c - \mathbf{F}_{\text{d1}}$$

(6-12)
\[
\frac{m \, dv_{b_2}}{dt} = b_2 - F^c - F_{d2}
\] (6-13)

The three terms on the right hand side of Eq. 6-12 and Eq. 6-13 correspond to the Brownian motion force, the elastic force and the drag force, respectively. The elastic force acting on both beads is the same in magnitude but opposite in direction since they are connected by the same spring. The drag force is written as negative by convention (positive \( F_d \) indicates deceleration). The relative velocity between the beads is:

\[
u = v_{b_2} - v_{b_1}
\] (6-14)

The relative velocity \( \mathbf{u} \) gives the rate of growth of \( \mathbf{R} \). Then, the deformation of the coil is given by:

\[
u = \frac{dr}{dt} = \dot{\mathbf{R}}
\] (6-15)

In order to have an equation for \( \mathbf{u} \), Eq. 6-12 is subtracted from Eq. 6-13 to obtain:

\[
\frac{m \, du}{dt} = (b_2 - b_1) - 2F^c - (F_{d2} - F_{d1})
\] (6-16)

Several assumptions are made at this point: (1) Inertia of the beads is negligible; (2) Hydrodynamic interactions are neglected. Hydrodynamic interactions are disturbances in the solvent velocity field created by the motion of one part of a polymer chain that can affect the drag exerted by the solvent on other parts of the same chain. In the case of the elastic dumbbell, the drag force exerted by one bead on the solvent will not affect the drag exerted by the solvent on the other bead. This means we are assuming that the coil is
'freely draining'.

Assuming the drag force is linearly related to the relative velocity between the beads and the fluid, using Eq. 6-6 and letting \( b = b_2 - b_1 \), we obtain:

\[
0 = b - 2H(R - R^*) - \zeta\left[u - (v(r + R) - v(r))\right] 
\]

(6-17)

where \( \zeta \) is the friction coefficient. For spherical beads, the friction coefficient is given by Stokes' law, \( \zeta = 6\pi \eta_r \), where \( r_0 \) is the bead radius and \( \eta_s \) is the solvent viscosity. The difference between the fluid velocity around the two beads can be expressed by a Taylor series based on the position of bead 1 and evaluated at bead 2. Then, we obtain:

\[
0 = b - 2H(R - R^*) - \zeta(R - R \cdot \nabla v) 
\]

(6-18)

When the equilibrium conformation is \( R^* = 0 \), the resulting equation is called Langevin's equation:

\[
0 = b - 2H(R - R^*) - \zeta(R - R \cdot \nabla v) 
\]

(6-19)

The first term on the right hand side of Eq. 6-19 corresponds to the Brownian forces. Their representation relies on the probability distribution of end-to-end vectors, \( \Psi(R) \). Using kinetic theory arguments it is possible to show that (91):

\[
b = -2kT \frac{\partial}{\partial R} \ln \Psi 
\]

(6-20)

where \( k \) is Boltzmann's constant; and \( T \) is absolute temperature. The notation \( \partial/\partial R \) is the gradient operator in \( R \) space (the configuration space of the molecule) (92).
The second term represents the elastic spring force, and the third term is the drag force, which is directly proportional to the difference between the rate of stretching of the spring $\dot{R}$ and that of the continuum fluid element containing the spring, $\mathbf{R} \cdot \nabla v$.

An interesting aspect of Langevin's equation is that it combines macroscopic forces (drag forces) with microscopic forces (Brownian forces and entropic forces). From a mathematical point of view, the link between these forces is the friction coefficient. In the hypothetical limit $\zeta \to 0$, Brownian motion and the entropic force control the coil deformation. At the other extreme, $\zeta \to \infty$, then $\mathbf{u} \to \mathbf{R} \cdot \nabla v$ which means that the two beads are separated at a rate equal to the fluid velocity difference; that is, the dumbbell deforms as a fluid element. In this case, it is said that the deformation is affine, and it is the fluid's macroscopic motion the phenomenon that controls the deformation.

Langevin's equation does not provide any information regarding the stress associated with the polymer. For this, $\langle \mathbf{R} \mathbf{R} \rangle$ needs to be found, and it is also necessary to know $\Psi(\mathbf{R})$. Such distribution is not a Gaussian distribution since the chain is no longer a random coil due to the deformation by the action of the forces in Eq. 6-16.

6.2.1. Equation of Continuity for $\Psi(\mathbf{R})$

When a dumbbell leaves one orientation, it has to end up in another orientation. This idea enables the set up of an equation of continuity for the distribution function (91). The result is:

$$\frac{\partial \Psi}{\partial t} + \frac{\partial}{\partial \mathbf{R}} (\mathbf{R} \Psi) = 0$$

(6-21)
Equation 6-19 is solved for $\dot{\mathbf{R}}$ and the result is substituted into Eq. 6-21,

$$\frac{\partial \Psi}{\partial t} + \frac{\partial}{\partial \mathbf{R}} \left( \mathbf{R} \cdot \nabla_{\mathbf{v}} \Psi - \frac{4kT\beta^2}{\zeta} \mathbf{R} \Psi - \frac{2kT}{\zeta} \frac{\partial}{\partial \mathbf{R}} \Psi \right) = 0$$

This equation is called Smoluchowski's equation. It is also called the diffusion equation (91). Its solution would yield the 'dynamic' probability distribution $\Psi(\mathbf{R})$ (with appropriate boundary and initial conditions). This equation also allows finding a governing equation for $\langle \mathbf{R} \rangle$, and in consequence a governing equation for the stress.

6.2.2. Dependence of Stress Tensor on Polymer Conformation

Multiplying Eq. 6-22 by $\mathbf{R} \langle \mathbf{R} \mathbf{R} \rangle$ and integrating over the $\mathbf{R}$ coordinates gives (93):

$$\frac{D \langle \mathbf{R} \mathbf{R} \rangle}{Dt} - \nabla_{\mathbf{v}} \cdot \langle \mathbf{R} \mathbf{R} \rangle - \langle \mathbf{R} \mathbf{R} \rangle \cdot \nabla_{\mathbf{v}} + \frac{8kT\beta^2}{\zeta} \langle \mathbf{R} \mathbf{R} \rangle - \frac{4kT}{\zeta} \mathbf{I} = 0$$

where $\mathbf{I}$ is the unit tensor; $D/Dt$ is the substantial time derivative defined by:

$$\frac{D \langle \mathbf{R} \mathbf{R} \rangle}{Dt} = \frac{\partial \langle \mathbf{R} \mathbf{R} \rangle}{\partial t} + \mathbf{v} \cdot \nabla \langle \mathbf{R} \mathbf{R} \rangle$$

Equation 6-24 means that we are following a specific particle and determining how its conformation changes with position and time.

Equation 6-23 can be written in a more compact form in terms of the upper-convected time derivative, defined in general as:

$$\mathbf{v} \mathbf{X} = \frac{DX}{Dt} - \nabla_{\mathbf{v}} \mathbf{X} - \mathbf{X} \cdot \nabla_{\mathbf{v}}$$
Then, Eq. 6-23 becomes:

\[
< \mathbf{R} \mathbf{R} >= \frac{-8kT\beta^2}{\zeta} < \mathbf{R} \mathbf{R} > + \frac{4kT}{\zeta} \mathbf{I} \tag{6-26}
\]

Multiplying Eq. 6-26 by \(2kTv\beta^2\) one obtains:

\[
\tau'_p = -\frac{8kT\beta^2}{\zeta} \tau'_p + \frac{8k^2T^2v\beta^2}{\zeta} \mathbf{I} \tag{6-27}
\]

At steady state and with no fluid motion, Eq. 6-27 predicts:

\[
\tau'_p = \nu k \Pi \tag{6-28}
\]

Equation 6-28 means that for no fluid deformation, there is a residual stress that is due to Brownian forces. In order to be consistent with the definition of stress, a new corrected stress tensor is defined, such that \(\tau = 0\) when \(\nu = 0\):

\[
\tau_p = \tau'_p - \nu k \Pi \tag{6-29}
\]

Substituting Eq. 6-11 into Eq. 6-29 gives:

\[
\tau_p = 2kTv\beta^2 < \mathbf{R} \mathbf{R} > - \nu k \Pi \tag{6-30}
\]

In a more general way:

\[
\tau_p = \nu < \mathbf{F}^c \mathbf{R} > - \nu k \Pi \tag{6-31}
\]

Equation 6-31 is called the Kramer’s form of the polymer contribution to the stress tensor (91). Another form of the polymer stress tensor is obtained by writing Eq. 6-26 as:
\[
<\mathbf{RR}>=-\frac{4}{\zeta}<\mathbf{F}^\mathbf{C}\mathbf{R}>+\frac{4kT}{\zeta}\mathbf{I}
\]  
(6-32)

Multiplying Eq. 6-32 by \(-\frac{\nu\zeta}{4}\) results in another way to express \(\tau_p\):

\[
\tau_p = -\frac{\nu\zeta}{4} <\mathbf{RR}>
\]  
(6-33)

Equation 6-33 is called the Giesekus' form of the polymer contribution to the stress tensor.

A constitutive equation for \(\tau_p\) is obtained after substituting Eq. 6-29 into Eq. 6-27.

\[
\tau_p + \frac{\zeta}{8kT\beta^2} \frac{\mathbf{E}}{\tau_p} = 2\left(\frac{n\zeta}{8\beta^2}\right)\mathbf{E}
\]  
(6-34)

where \(\mathbf{E}\) is the rate of deformation tensor: \(\mathbf{E} = \frac{1}{2}(\nabla\mathbf{v} + \nabla\mathbf{v}^\top)\). If we define the polymer relaxation time by:

\[
\dot{\lambda} = \frac{\zeta}{8kT\beta^2} = \frac{\zeta}{4H}
\]  
(6-35)

and a viscosity due to the polymer by:

\[
\eta_p = \frac{\nu\zeta}{8\beta^2}
\]  
(6-36)

The final equation is:

\[
\tau_p + \dot{\lambda} \tau_p = 2\eta_p \mathbf{E}
\]  
(6-37)
The total stress tensor is obtained by adding the contributions of solvent and polymer:

\[ \tau = \tau_s + \tau_p \]  

(6-38)

For a Newtonian solvent, \( \tau_s = 2\eta_s E \). Equation 6-38 assumes that the polymer solution is dilute.

When substituting Eq. 6-38 into Eq. 6-37, the result is equivalent to the so-called Oldroyd-B constitutive equation. This is a simple but qualitatively useful constitutive equation for dilute solutions of macromolecules (90).

6.3. Non-Hookean Elastic Dumbbells

The rheological data for dilute solutions indicates that the Hookean dumbbell suspension gives steady state shear flow material functions that are independent of the shear rate, and also a steady state elongational viscosity that goes to infinity at a finite strain rate (91). It has been shown that the main limitation of the Hookean dumbbell (or the Oldroyd-B) model is that it allows for infinite extension, which is objectionable for large molecular extensions (90). In what follows, two models are presented that impose a restriction regarding the extensibility of the polymer molecules.

6.3.1. FENE Dumbbell Model

One of the simplest models for representing a flexible macromolecule with a finite limit of extensibility is the Warner’s finitely extensible nonlinear elastic (FENE) dumbbell model (94). It consists of two beads connected by a spring whose connector force law is:
Here, $R^2$ is the trace of $RR$ ($R^2 = \text{tr} RR$); $R_o = N_0 b_k$ is the fully extended length of the molecule. A similar procedure to that done with the elastic dumbbell model needs to be done here in order to obtain a constitutive equation for the polymer stress tensor.

Writing Eq. 6-22 in terms of $F^C$, we have:

$$\frac{\partial \Psi}{\partial t} + \frac{\partial}{\partial R} \left( R \cdot \nabla \Psi - \frac{2}{\zeta} F^c \Psi - \frac{2kT}{\zeta} \frac{\partial}{\partial R} \Psi \right) = 0$$

(6-40)

Substitution of Eq. 6-39 into Eq. 6-40 results into a non-linear equation from which is not possible to obtain a direct solution. Therefore, it is necessary to explore if a modification can be introduced to make the model more tractable. If Eq. 6-39 is substituted into Eq. 6-31, the following results:

$$\tau_p = \nu H \left( \frac{RR}{1-R^2 / R_o^2} \right) - \nu kT$$

(6-41)

Peterlin (95) suggested to approximate Eq. 6-41 as:

$$\tau_p = \nu H \frac{<RR>}{1-<R^2 / R_o^2>} - \nu kT$$

(6-42)

Then, the equation for the force law of the spring is now:

$$F^c = \frac{HR}{1-<R^2 / R_o^2>}$$

(6-43)

A spring described by this approximation (Eq. 6-43) is called a FENE-P spring (94).
The goal at this point is to obtain a constitutive expression equivalent to Eq. 6-37 using Eq. 6-43. Taking the trace of Eq. 6-42 and using tr $<\mathbf{R}\mathbf{R}> = <\mathbf{R}^2> = R_0^2 <\mathbf{R}^2 / R_0^2 >$ gives:

$$\text{tr} \tau_p = vH R_0^2 \frac{<\mathbf{R}^2 / R_0^2 >}{1 - <\mathbf{R}^2 / R_0^2 >} - 3vkT$$ (6-44)

From Eq. 6-44 the following is obtained:

$$<\mathbf{R}^2 / R_0^2 > = 1 - \frac{1}{Z(\text{tr} \tau_p)}$$ (6-45)

Here

$$Z(\text{tr} \tau_p) = 1 + \frac{3}{L^2} \left( 1 + \frac{\text{tr} \tau_p}{3vkT} \right)$$ (6-46)

where $L^2 = \frac{HR_0^2}{kT} = 3 \frac{R_0^2}{R_{eq}^2}$. Then, combining Eq. 6-45 and Eq. 6-43 one obtains:

$$\mathbf{F}^C = HZ \mathbf{R}$$ (6-47)

Combining Eq. 6-47 and Eq. 6-31 an expression for $\tau_p$ results:

$$\tau_p = vHZ <\mathbf{R}\mathbf{R}> - vkTI$$ (6-48)

Now, $<\mathbf{R}\mathbf{R}>$ can be eliminated between Eq. 6-48 and Eq. 6-33 to obtain (94):

$$Z\tau_p + \lambda \tau_p - \lambda(\tau_p + vkTI) \frac{D\ln Z}{Dt} = 2vkT\lambda \mathbf{E}$$ (6-49)

This equation is nonlinear in stress due to the dependence of $Z$ on $\tau_p$. When $L \to \infty$, ...
$Z=1$, so Eq. 6-43 simplifies to Eq. 6-4 and the rheological equation of state for Hookean dumbbells (Eq. 6-37) is obtained (94), which means that the dumbbells will have infinite extensibility. Equation 6-37 is also obtained more directly if $Z=1$ is substituted into Eq. 6-49. On the other hand, when $L \to 0$, the equation of state for a rigid rod is obtained.

6.3.2. Lhuillier's Model

Lhuillier (30) proposed a new dumbbell-like model in which the finite extensibility is considered through a progressive modification of the hydrodynamic interactions and of the diffusion processes as the polymer stretches. The starting point of the model is a general form of the evolution equation for $R$ given by (96):

$$\frac{dR}{dt} = W \times R + A(R) : E - D(R) \frac{\partial \phi^*}{\partial R}$$ (6-50)

The first two terms on the right-hand side in Eq. 6-50 represent the distortion rate induced by the external flow $v$, split into a contribution by a rotation rate $W = (1/2)V \times v$, and the rate of deformation tensor $(E)$. The tensor $A$ is a third-order tensor representing the fact that even though the polymer rotates with the fluid, it is not affinely deformed by the strain rate due to hydrodynamic interactions between the monomers. The last term represents two effects: a restoring mechanism and the effect of Brownian motion. It is expressed with a diffusion tensor $D$ depending on the distortion, multiplied by a force involving $\phi^*$ (non-dimensional free-energy of the chain) which is:

$$\phi^* = \frac{\phi}{kT} + \ln \Psi$$ (6-51)
where $\phi$ is the energy of distortion.

Equation 6-50 is equivalent to Eq. 6-19. To visualize it better, Eq. 6-19 can be written as:

$$\frac{d\mathbf{R}}{dt} = \mathbf{R} \cdot \nabla v - \frac{2}{\zeta} \mathbf{F}^c - \frac{2kT}{\zeta} \frac{\partial}{\partial \mathbf{R}} \ln \Psi$$

(6-52)

The first two terms on the right hand side of Eq. 6-50 are equivalent to the first term in Eq. 6-52, whereas the last term in Eq. 6-50 comprising the spring restoring force and the effect of Brownian motion is equivalent to the last two terms of Eq. 6-52.

The goal is to find appropriate forms for $A$ and $D$ such that Eq. 6-50 results into an evolution equation that fully accounts for finite extensibility. The resulting equation is (30):

$$\frac{d\mathbf{R}}{dt} = \mathbf{W} \times \mathbf{R} + \left( a^*(R) I - F(R) \frac{\mathbf{R} \mathbf{R}}{\text{tr} \mathbf{R}} \right) \left( \mathbf{e} \cdot \mathbf{R} - D \frac{\partial \phi}{\partial \mathbf{R}} \right)$$

(6-53)

with

$$D = \frac{2kT}{\zeta} \geq 0, \quad a^*(R) = a + (1 - a) F(R), \quad 0 \leq a \leq 1,$$

and

$$0 \leq F(R) \leq 1, \quad \frac{\partial F}{\partial R} \geq 0 \text{ and } F(R, t) = 1$$

The constant $D$ is called the rotatory diffusivity of the dumbbell, which is the rate at which a particle reorients by Brownian motion (90); $\alpha$ is a constant factor indicating the
relative efficiency of the fluid strain rate to deform the polymer (Gordon-Schowalter coefficient). The function $F(R)$ is where the main difference with the FENE model resides. The finite extensibility in the FENE model is expressed only through the connector force, but in this new model it is also contained in $F(R)$, which not only expresses the saturation of the polymer distortion, but also the modifications of the hydrodynamic interactions and the relative intensity of the diffusion processes (diffusion due to orientation and diffusion due to stretch). It can also be considered as some mean percentage of straight segments in the polymer chain. This means that pulling on the chain is resisted by the fraction $1 - F$ of coiled parts (30).

As it was done before for Hookean dumbbells and for FENE dumbbells, an equation for $\langle RR\rangle$ can be deduced after multiplying the evolution equation for $R$ (Eq. 6-53) by $RR$ and integrating over the space of conformations. The following final set of dimensionless equations is obtained (30):

$$\dot{\lambda} \mathbf{S} = -\lambda (1 - \langle a^* \rangle) (\mathbf{S} \cdot \mathbf{E} + (\mathbf{S} \cdot \mathbf{E})^\top) + \langle a^* \rangle \mathbf{l} - \left[ \alpha_{eq} + \frac{2\lambda}{L^2} \mathbf{S} : \mathbf{E} \right] \mathbf{S}$$  \hspace{1cm} (6-54)

and

$$\tau = 2\eta_0 \mathbf{E} + \nu kT \lambda \mathbf{S}$$  \hspace{1cm} (6-55)

with

$$\langle a^* \rangle = a + (1 - a) \frac{\text{tr} \mathbf{S}}{L^2}$$  \hspace{1cm} (6-56)

and
The dimensionless conformation tensor is defined by:

$$a^*_{eq} = a + (1 - a) \frac{R^2_{eq}}{R_0^2} \quad (6-57)$$

The dimensionless conformation tensor is defined by:

$$S = 3 \frac{<RR^*>}{R_{eq}^2} \quad (6-58)$$

Notice that the expression for the stress tensor (Eq. 6-55) is equivalent to Eq. 6-38.

The second term in Eq. 6-55 \((\dot{\gamma})\) is written in the Giesekus' form.

6.4. Hydrodynamic Interactions

An assumption considered in Langevin's equation and in the FENE-P model is that the two beads of the dumbbell move through the solvent without disturbing the velocity field. One way to remove this "free-draining" assumption is to start by assuming that a force \(F\) is exerted by a bead on a Newtonian solvent at the origin. The force sets the surrounding solvent in motion, such that the velocity away from the origin at a point \(r\) is given by the steady-state value (90):

$$v' = \mathbf{\Omega} \cdot \mathbf{F} \quad (6-59)$$

where \(\mathbf{\Omega}\) is the Oseen tensor:

$$\mathbf{\Omega}(r) = \frac{1}{8\pi \eta \tau} \left( 1 + \frac{rr}{r^2} \right) \quad (6-60)$$

The influence of a force applied at a point in the solvent decays as \(1/r\) as the distance \(r\) from the point increases. This decay is gradual, and then the drag force exerted by a bead on the solvent is transmitted to a large volume containing other beads. This tensor is a
good approximation at distances that are large compared to the bead diameter, whereas it
is inaccurate close to the bead (93).

In order to account for hydrodynamic interactions, the fluid velocity at the bead
location \(r=r_i\) is given by: \(v_i = v_{i0} + v_i\). Here, \(v_{i0}\) is the velocity of the fluid at \(r_i\) in the
absence of any beads, and \(v_i\) is the contribution from the other bead to the velocity of the
solvent at \(r_i\). The disturbance \(v_i\) is given by Eq. 6-59. This change is introduced into the
force balance for each bead with care regarding the consistency of the signs. After doing
this, Eq. 6-19 now becomes:

\[
0 = (\zeta \Omega + \lambda) \cdot (b - 4kT\beta^2 R) - \zeta (R - \nabla v)
\]  

(6-61)

Now, Eq. 6-61 is solved for \(\dot{R}\) and the result is substituted into Eq. 6-21. Then, after
multiplying by \(RR\) and integrating over the \(R\) coordinates, the following is obtained:

\[
<\dot{RR}> + (\zeta \Omega + \lambda) \left( \frac{8kT\beta^2}{\zeta} <RR>-\frac{4kT}{\zeta}I \right) = 0
\]  

(6-62)

Notice that when \(\Omega=0\) in Eq. 6-62, Eq. 6-26 is recovered.

Unfortunately, there is not a big improvement in the predictions by using this
approach (91). It should be clear by now that the hydrodynamic force should change as
the polymer changes its configuration from random coil at equilibrium to more elongated
shapes. The hydrodynamic friction coefficient should be shape-dependent. In order to
keep the simplicity of the original dumbbell model, a friction law can be assigned such
that it allows for frictional changes that correspond to the complete transition from a
random coil to a highly extended chain (97). The most commonly adopted model is due to Hinch and de Gennes. This model assumes that the frictional interaction remains isotropic, but with a magnitude of the friction coefficient on the beads that depends linearly upon the end-to-end length of the dumbbell (97):

$$\zeta = \zeta_0 \sqrt{1 \over 3} \text{tr} \mathbf{S}$$  \hspace{1cm} (6-63)

Here, $\zeta_0$ is the friction coefficient when the molecule is at equilibrium. At equilibrium, $\text{tr} \mathbf{S} = 3$, since $\text{tr} <\mathbf{R}\mathbf{R}^T> = R_{eq}^2$ (see Eq. 6-58).

6.5. Application of Models to Shear and Extensional Flows

In this section, we will explore the prediction of the models presented above in simple shear flow and uniaxial extensional flow. This will help to establish comparisons among them and to explore their strengths and weaknesses.

6.5.1. Langevin’s Equation for Extensional Flow

For steady uniaxial extensional flow, in cylindrical coordinates, we have the velocity field: $v_z = \dot{\varepsilon} z$, $v_r = -1/2 \dot{\varepsilon} r$. $v_\theta = 0$, where $\dot{\varepsilon}$ is the strain rate. Langevin’s equation is a good starting point to visualize the changes in conformation of a dumbbell when subjected to a particular flow. Some modifications will be introduced: (1) only extension along the $z$ direction is considered; (2) Brownian motion will not be considered; (3) the equilibrium conformation of the dumbbell will be an arbitrary $\mathbf{R} = \mathbf{R}^*$. Thus, we will use Eq. 6-18 with $b=0$. 
$$0 = -2H(R - R^*) - \zeta(\dot{\gamma} - R \cdot \nabla \gamma)$$  \hspace{1cm} (6-64)

For extension only in the $z$ direction, Eq. 6-64 yields:

$$\frac{DR_z}{Dt} = R_z \frac{\partial \gamma_z}{\partial z} - \frac{2H}{\zeta} (R_z - R_z^*)$$  \hspace{1cm} (6-65)

with initial condition: $t=0$, $R_z = R_z^*$.

The left-hand side of Eq. 6-65 is a substantial time derivative (Eq. 6-24). This problem is considered to be at steady-state, which means that all the dumbbells that pass through a fixed point will have the same value $R_z$ at all times. However, if we are following a specific dumbbell, the value $R_z$ varies as the dumbbell moves.

In order to make the problem more tractable, it is convenient to make Eq. 6-65 and the initial condition dimensionless. The following dimensionless variables are introduced:

$$S = \frac{R_z}{R_z^*}, \quad t' = \frac{t}{t_{char}}$$  \hspace{1cm} (6-66a, 6-66b)

Substitution of the dimensionless variables into Eq. 6-65 gives:

$$\frac{R_z^*}{t_{char}} \frac{DS}{Dt'} = R_z^* S \dot{\gamma} - \frac{2H}{\zeta} R_z^* (S - 1)$$  \hspace{1cm} (6-67)

If we consider that the characteristic time for this experiment is of the order of the inverse of the strain rate ($t_{char} \dot{\gamma} \approx 1$), Eq. 6-67 becomes:

$$\frac{DS}{Dt'} = S - \frac{t_{char}}{2\lambda} (S - 1)$$  \hspace{1cm} (6-68)
Figure 6.4. Dimensionless dumbbell length in uniaxial extensional flow as a function of dimensionless time for different values of $De_{\text{ext}}$. Calculated with Langevin’s equation.

Here, $\lambda$ is given by Eq. 6-35. The factor $\frac{t_{\text{char}}}{\lambda}$, the ratio between the characteristic time of the experiment and the relaxation time (characteristic time of the polymer) can be expressed as $\frac{1}{2De_{\text{ext}}}$ where $De_{\text{ext}}$ is the Deborah number for uniaxial extensional flow.

Therefore, Eq. 6-68 becomes:

$$\frac{DS}{Dt'} = S - \frac{1}{2De_{\text{ext}}}(S - 1) \quad (6-69)$$

with the initial condition: $t' = 0, S = 1$.

This expression will tell us that the dumbbells can be infinitely stretched as shown in Fig. 6.4. In this graph, the dimensionless extension in $x$ is represented as a function of $t'$. 
for several values of $De_{\text{ext}}$. This result makes no physical sense, since the random coil the dumbbell represents has a finite length. For this reason, finite extensibility of the dumbbell is a necessary condition towards a model that approaches reality satisfactorily.

![Graph showing dimensionless dumbbell length in uniaxial extensional flow as a function of dimensionless time for different values of $De_{\text{ext}}$.](image)

Figure 6.5. Dimensionless dumbbell length in uniaxial extensional flow as a function of dimensionless time for different values of $De_{\text{ext}}$. Calculated with Langevin’s equation accounting for finite extensibility (The maximum dimensionless length of the dumbbell is $L=100$).

In order to consider a dumbbell with finite extensibility, $H$ in Eq. 6-64 can be replaced by $\frac{H}{1-<R^2_z/R^2_0>}$ as stated above for the FENE model. A new dimensionless expression for $S$ is obtained:

$$\frac{DS}{Dt'} = S - \frac{1}{2De_{\text{ext}}(1 - S^2/L^2)}(S-1)$$

(6-70)
where $L^2 = \frac{R_0^2}{(R^*)^2}$. For consistency in the notation, $(R^*)^2 = \frac{S^2}{3}$. Figure 6.5 shows a plot of $S$ vs. $t'$, where it is clearly shown that $S$ can never reach values greater or equal to $L$ (maximum dimensionless length, $L=100$). One can intuitively predict this sort of behavior by noticing that as $S$ approaches $L$, the last term on the right hand side of Eq. 6-70 becomes larger. This term represents the force exerted by the spring against being stretched by the flow, or in other words, against being stretched affinely with the fluid. Figure 6.6 shows a plot of $S_{\text{max}}$ as a function of $De_{\text{ext}}$ for several values of $L$. At low $De_{\text{ext}}$, the values of $S_{\text{max}}$ remain nearly the same for every $L$, but when $De_{\text{ext}}$ is close to 0.4, $S_{\text{max}}$ increases, until it finally reaches a plateau as it approaches the corresponding value of $L$.

![Figure 6.6. Maximum dimensionless dumbbell length in uniaxial extensional flow as a function of $De_{\text{ext}}$ for different values of $L$. Calculated with Langevin's equation accounting for finite extensibility.](image-url)
6.5.2. FENE-P Dumbbell Model

6.5.2.1. Steady Shear Flow

For steady shear flow (Couette flow) the velocity field is: $v_x = \dot{y}$. Also $\tau_{yy} = \tau_{xx} = 0$. Equation 6-49 gives (94):

$$Z_{xx} - 2\lambda_{pxx} \dot{\gamma} = 0 \quad (6-71)$$

$$Z_{pxx} = \nu k T \lambda \dot{\gamma} \quad (6-72)$$

Let us introduce the following variables: $M = T_{pxx} / 3\nu k T$. $G = T_{pxx} / 3\nu k T$ and $De_{shear} = \lambda \dot{\gamma}$ where $De_{shear}$ is the Deborah number (notice that $\lambda$ is a characteristic time for the dumbbell and $\dot{\gamma}$ is the inverse of the characteristic time of the experiment).

Substitution into Eq. 6-71 and Eq. 6-72 yields:

$$\left[ 1 + \frac{3}{L^2} (1 + M) \right] M = 2 De_{shear} G \quad (6-73)$$

$$\left[ 1 + \frac{3}{L^2} (1 + M) \right] G = \frac{1}{3} De_{shear} \quad (6-74)$$

These two equations give:

$$M = 6G^2 \quad (6-75)$$

$$G^3 + 3pG + 2q = 0 \quad (6-76)$$
where \( p = \frac{L^2 + 3}{54} \) and \( q = -De_{\text{shear}} \frac{L^2}{108} \). The only real solution of Eq. 6-76 is:

\[
G = \frac{-p}{(-q + \sqrt{p^3 + q^2})^{1/3}} + \left( -q + \sqrt{p^3 + q^2} \right)^{1/3} \tag{6-77}
\]

Expanding Eq. 6-77 in a Taylor series, it is possible to obtain for \( De_{\text{shear}} \to 0 \ (\dot{\gamma} \to 0) \):

\[
G = \frac{\tau_{\text{pex}}}{3vKT} = \frac{1}{3} \frac{L^2}{L^2 + 3} De_{\text{shear}} \tag{6-78}
\]

Rearranging Eq. 6-78 and substituting the definition for \( De_{\text{shear}} \), the following is obtained:

\[
\tau_{\text{pex}} = vKT\lambda \frac{L^2}{L^2 + 3} \dot{\gamma} \tag{6-79}
\]

Notice that Eq. 6-79 is of the form \( \tau = \eta \dot{\gamma} \). Therefore, when \( \dot{\gamma} \to 0 \):

\[
\eta_p = vKT\lambda \frac{L^2}{L^2 + 3} \tag{6-80}
\]

where \( \eta_p \) is the contribution of the polymer to the solution viscosity \( \bar{\eta} \), which is defined as:

\[
\bar{\eta} = \eta_s + \eta_p \tag{6-81}
\]

Then, Eq. 6-80 can be written as:

\[
\left( \eta - \eta_s \right)_{\dot{\gamma} \to 0} = \left( \eta_0 - \eta_s \right) = vKT\lambda \frac{L^2}{L^2 + 3} \tag{6-82}
\]

In order to determine how the viscosity of the solution varies with \( De_{\text{shear}} \) according
to this model, we have from the definition of $G$:

$$\frac{\tau_{pys}}{D_{\text{shear}}} = 3\nu k T \frac{G}{D_{\text{shear}}}. \quad (6-83)$$

Equation 6-83 can be written as:

$$\frac{\tau_{pys}}{\gamma} = 3\nu k T \frac{G}{D_{\text{shear}}} = \eta_p \quad (6-84)$$

Combining Eq. 6-81, Eq. 6-82 and Eq. 6-84 results into:

$$\frac{\eta - \eta_s}{\eta_0 - \eta_s} = \frac{3}{L^2} \frac{L^2 + 3}{L^2} \frac{G}{D_{\text{shear}}} \quad (6-85)$$

Figure 6.7 shows how the normalized shear viscosity calculated with Eq. 6-85 varies with $D_{\text{shear}}$ for different values of $L$. Clearly, the model predicts a shear-thinning behavior whose onset in terms of, $D_{\text{shear}}$, increases with coil length. At high values of $D_{\text{shear}}$, it can be shown that Eq. 6-85 reduces to the asymptotic behavior:

$$\frac{\eta - \eta_s}{\eta_0 - \eta_s} = 3 \left( \frac{L^2}{L^2} \right)^{1/3} \frac{G}{D_{\text{shear}}} \quad (6-86)$$

so that the slopes of the three curves in Fig. 6.7 at high $D_{\text{shear}}$ are all the same.

The first and second normal stress coefficients due to the polymer are defined respectively as:

$$\psi_1 = \frac{\tau_{pys} - \tau_{pyy}}{\gamma^2} \quad (6-87)$$
From Eq. 6-87 and Eq. 6-88, we find:

\[ \psi_z = \frac{\tau_{yy} - \tau_{zz}}{\gamma^2} \]  \hspace{1cm} (6-88)

and

\[ \psi_1 = \frac{2}{\nu k T} (\eta - \eta_s)^2 \]  \hspace{1cm} (6-89)

and

\[ \psi_2 = 0 \]  \hspace{1cm} (6-90)

Figure 6.7. Normalized viscosity in shear flow as a function of $De_{shear}$. Calculated with FENE-P dumbbell model for different values of $L$. 
The relative dumbbell elongation $<R^2/R_0^2>$ as a function of $De_{shear}$ is calculated from Eq. 6-45, where: $Z = 1 + \frac{3}{L^2}(1 + 6G^2)$ and $G$ is calculated from Eq. 6-77. Notice that in this case we are considering the changes in the size of the dumbbell treating the problem in three dimensions ($R^2 = \text{tr} <RR>$). The results are shown in Fig. 6.8, where very high values of $De_{shear}$ are necessary to almost fully stretch the dumbbells. One would not expect to be physically possible to fully extend the dumbbells in shear flow. Looking at Fig. 6.7 and Fig. 6.8, notice that the onset of shear-thinning occurs when the dimensions of the dumbbell start to change. In shear, the dumbbells orient and stretch. The results in these plots suggest that the decrease in viscosity is a consequence of such orienting-stretching phenomenon, which favors a decrease in flow resistance.

Figure 6.8: Relative dumbbell elongation in shear flow as a function of $De_{shear}$ Calculated with FENE-P dumbbell model for different values of $L$. 
6.5.2.2. Steady Uniaxial Extensional Flow

For steady uniaxial extensional flow in cylindrical coordinates, Eq. 6-49 gives (94):

\[ Z\tau_{rr} + \lambda \dot{e} \tau_{rr} = -\nu k T \lambda \dot{e} \]  
(6-91)

\[ Z\tau_{\rho\theta} + \lambda \dot{e} \tau_{\rho\theta} = -\nu k T \lambda \dot{e} \]  
(6-92)

\[ Z\tau_{zz} - 2\lambda \dot{e} \tau_{zz} = 2\nu k T \lambda \dot{e} \]  
(6-93)

From Eq. 6-91 and Eq. 6-92: \( \tau_{rr} = \tau_{\rho\theta} \). Then, this system simplifies into two equations, one for \( \tau_{rr} \) and one for \( \tau_{zz} - \tau_{rr} \):

\[ [1 + 5(1 + A0) \frac{B}{3} e^N] = D e^P \]  
(6-94)

\[ [1 + 5(1 + A0) \frac{B}{3} e^N] = 0 \]  
(6-95)

where: \( B = 3/L^2 \), \( N = \text{tr} \tau_p / 3\nu k T \), \( P = (\tau_{zz} - \tau_{rr}) / 3\nu k T \) and \( D e^P = \lambda \dot{e} \). From Eq. 6-94 and Eq. 6-95 a quadratic equation in \( D e^P \) is obtained (94):

\[ C_1 D e^2 + C_2 D e + C_3 = 0 \]  
(6-96)

where

\[ C_1 = 2BP \]  
(6-97)

\[ C_2 = -5B^2 P^2 + BP(1 - B) + B \]  
(6-98)

\[ C_3 = 2B^3 P^3 - (B + 1)(BP - B^2 P^2) \]  
(6-99)

The contribution of the polymer to the extensional viscosity is found from the
definition of \( P \):

\[
\frac{\tau_{\text{pass}} - \tau_{\text{ext}}}{\dot{\varepsilon}} = 3 k T \lambda \frac{P}{D_{\text{ext}}} = \eta_p
\]  

(6-100)

In order to find the total viscosity of the polymer solution, it is necessary to know the viscosity of the solvent. Consider a Newtonian fluid subjected to uniaxial extension. After performing a force balance on a cylindrical fluid element (problem posed in cylindrical coordinates) the conclusion is:

\[
\eta_{\text{m}} = 3 \eta_s
\]  

(6-101)

Equation 6-101 means that the apparent viscosity of a Newtonian fluid under uniaxial extension, \( \eta_{\text{m}} \) (or elongational viscosity) is 3 times the viscosity that one would observe when subjecting the same Newtonian fluid to a simple shear flow. Equation 6-101 is known as the Trouton's ratio. Therefore, the apparent viscosity of a solution subjected to uniaxial extension is:

\[
\tilde{\eta} = 3 \eta_s + \eta_p
\]  

(6-102)

Combining Eq. 6-82, Eq. 6-100 and Eq. 6-102, one obtains:

\[
\frac{\tilde{\eta} - 3 \eta_s}{3(\eta_o - \eta_s)} = \frac{L^2 + 3}{L^2} \frac{P}{D_{\text{ext}}}
\]  

(6-103)

Equation 6-103 is a normalized apparent viscosity. This normalization is made considering that as \( D_{\text{ext}} \to 0 \), the ratio approaches 1. The parameter \( P \) is obtained from Eq. 6-96. A plot of \( P \) vs. \( D_{\text{ext}} \) for the two solutions of Eq. 6-96 suggests that we consider
the solution with the plus sign for $\text{De}_{\text{ext}}<1$ to avoid having a negative $\bar{\eta}$, whereas the minus sign makes physical sense for $\text{De}_{\text{ext}}>1$.

Results from Eq. 6-103 are shown in Fig. 6.9. This figure shows how the normalized apparent viscosity of the solution varies as $\text{De}_{\text{ext}}$ increases. For all values of $L$, the critical value of $\text{De}_{\text{ext}}$ for the sudden increase in viscosity is close to 0.5. Such an increase is very dramatic as evidenced by a change of several orders of magnitude in the normalized viscosity. From this result, it is also concluded that Trouton’s rule only holds for relatively low values of $\text{De}_{\text{ext}}$ where the polymeric solutions behave nearly as Newtonian fluids.

![Figure 6.9. Normalized viscosity in uniaxial extensional flow as a function of $\text{De}_{\text{ext}}$. Calculated with FENE-P dumbbell model for different values of $L$.](image-url)
Figure 6.10. Relative dumbbell elongation in uniaxial extensional flow as a function of $De_{ext}$
Calculated with FENE-P dumbbell model for different values of $L$.

The relative dumbbell elongation $< R^2 / R_0^2 >$ as a function of $De_{ext}$ is calculated from Eq. 6-45, where: $Z = 1 + \frac{3}{L^2}(1 + N)$ and $N$ is calculated from Eq. 6-94. Figure 6.10 shows how the relative elongation changes with $De_{ext}$. There is a specific critical value of $De_{ext}$ at which the dumbbells undergo sudden extension, until at high values, and due to the finite extensibility character of the model, the relative elongation reaches a plateau. This critical value of $De_{ext}$ corresponds to the same value at which the viscosity of the solution increases. This means that the departure from Newtonian behavior is caused by the extension of the dumbbells. For $De_{ext}$ not high enough to promote stretching of the molecules, these remain coiled and the friction with the solvent is minimum, but as the coils begin to stretch, friction with the solvent increases and so does the apparent
viscosity of the solution. It is important to emphasize at this point that with the experimental set up described in the previous chapters it is not possible to account for these sudden changes in apparent viscosity. The set up allows us to quantify the resistance of the solution to flow through the capillaries considering the whole region between them. However, the stretching of the molecules (coil-stretch transition) occurs in a very small fraction of that region. Thus, the local flow resistance is negligible to the sensitivity of the apparatus.

6.5.3. Lhuillier's Model

6.5.3.1. Steady Shear Flow

The simple shear flow problem to be studied is the same as in section 6.5.2.1. First, it is necessary to set up the proper equations for this flow using Eq. 6-54. In this case, the substantial derivative is: \( \frac{\mathrm{DS}}{\mathrm{Dt}} = 0 \). In simple shear, a dumbbell will orient, adopting a specific conformation which will remain unaltered as it travels with the flow.

The following set of algebraic equations is obtained from Eq. 6-54:

\[
-2D_{\text{shear}} S_{yx} = -D_{\text{shear}} (1 - <a^*>)S_{yx} + <a^*> - \left( a_{eq}^* + \frac{2}{L^2} D_{\text{shear}} S_{yx} \right) S_{xx}
\]  

\( (6-104) \)

\[
0 = -D_{\text{shear}} (1 - <a^*>)S_{yx} + <a^*> - \left( a_{eq}^* + \frac{2}{L^2} D_{\text{shear}} S_{yx} \right) S_{yy}
\]  

\( (6-105) \)

\[
0 = <a^*> - \left( a_{eq}^* + \frac{2}{L^2} D_{\text{shear}} S_{yx} \right) S_{zz}
\]  

\( (6-106) \)
The viscosity of the solution is found using Eq. 6-55. We have:

\[
\begin{align*}
\tau_{yx} &= 2\eta_s E_{yx} - \nu k T\lambda S_{yx} \\
\end{align*}
\]  

(6-108)

where \( E_{yx} = \frac{1}{2} \dot{\gamma} \) and \( S_{yx} = -\dot{\gamma} S_{yy} \). Therefore, Eq. 6-108 yields:

\[
\dot{\tau}_{yx} = \eta_s \dot{\gamma} + \nu k T\lambda \dot{\gamma} S_{yy}
\]  

(6-109)

Rearranging Eq. 6-109 gives:

\[
\frac{\dot{\tau}_{yx}}{\dot{\gamma}} = \eta_s + \nu k T\lambda S_{yy} = \eta
\]  

(6-110)

Combining Eq. 6-110 and Eq. 6-81 gives:

\[
\eta_p = \nu k T\lambda S_{yy}
\]  

(6-111)

In order to find an analytical expression for the zero-shear viscosity, we need the value of \( S_{yy} \) when \( D_{shear} \to 0 \). A regular perturbation expansion of \( S_{ij} \) in \( D_{shear} \) is done, and for \( S_{ij} \) one obtains:

\[
S_{ij} = S_{ij}^{(0)} + S_{ij}^{(1)} D_{shear} + S_{ij}^{(2)} D_{shear}^2 + \ldots
\]  

(6-112)

Equation 6-112 is then plugged into Eqs. 6-104 to 6-107. Solving, we get \( S_{yy}^{(0)} = 1 \) and \( S_{yy}^{(1)} = 0 \). Then, Eq. 6-111 becomes for \( D_{shear} \to 0 \):
Figure 6.11. Normalized viscosity in shear flow as a function of $D_{e,\text{shear}}$. Calculated with Lhuillier’s dumbbell model for different values of $\alpha$. The maximum dimensionless length of the dumbbell is $L=100$.

Solutions for all other values of $D_{e,\text{shear}}$ are found numerically. Combining Eq. 6-111 and Eq. 6-113, we get:

$$\frac{\eta - \eta_s}{\eta_0 - \eta_s} = S_{\eta}$$  \hspace{1cm} (6-114)

Figure 6.11 shows how the normalized shear viscosity (Eq. 6-114) varies with $D_{e,\text{shear}}$ and with $\alpha$. If $\alpha=1$ is used in the above set of equations, the system has no solution. The necessary condition is $\alpha < 1 - \frac{1}{L^2}$ (30). The model predicts shear thinning, but instead of decreasing continuously as $D_{e,\text{shear}}$ increases, the viscosity reaches a plateau at
approximately $De_{\text{shear}} = 1/(1+a)$. The shear thinning behavior strongly depends on $a$. For low values of $a$ up to approximately 0.4, shear thinning is observed from relatively low values of $De_{\text{shear}}$. As $a$ increases, the onset of shear thinning increases, as well as the range of $De_{\text{shear}}$ in which the viscosity decreases. This is the behavior observed in Fig. 6.12, where a plot of the relative dumbbell elongation ($tr S/L^2$) vs. $De_{\text{shear}}$ shows that as $a$ increases, the departure from the equilibrium conformation is larger when comparing equal values of $De_{\text{shear}}$.

![Figure 6.12](image)

Figure 6.12. Relative dumbbell elongation in shear flow as a function of $De_{\text{shear}}$. Calculated with Lhuillier's dumbbell model for different values of $a$. The maximum dimensionless length of the dumbbell is $L=100$.

### 6.5.3.2. Steady Uniaxial Extensional Flow

This problem is the same as the problem in section 6.5.2.2. Using Eq. 6-54 the following system of equations is obtained:
\[ D_{e,x}(\frac{DS_{zz}}{Dt'} - 2S_{zz}) = -2D_{e,x}S_{zz}(1- <a*>)+ <a*> - \left( a_{eq}^{*} + \frac{2}{L^2} D_{e,x} S \right) S_{zz} \]  \hfill (6-115)

\[ D_{e,n}(\frac{DS_{nn}}{Dt'} - S_{nn}) = D_{e,n}S_{n}(1- <a*>)+ <a*> - \left( a_{eq}^{*} + \frac{2}{L^2} D_{e,n} S \right) S_{nn} \]  \hfill (6-116)

\[ D_{e,\theta \theta}(\frac{DS_{\theta \theta}}{Dt'} - S_{\theta \theta}) = D_{e,\theta \theta}S_{\theta \theta}(1- <a*>)+ <a*> - \left( a_{eq}^{*} + \frac{2}{L^2} D_{e,\theta \theta} S \right) S_{\theta \theta} \]  \hfill (6-117)

As before, \( t' \) is a dimensionless time given by Eq. 6-66b; the characteristic time is chosen such that \( t'_{\text{char}} \approx 1 \), and \( D_{e,x} \) is defined as before \( (D_{e,x} = \frac{\dot{\lambda}}{t_{\text{char}}}) \). We also have: \( S = S_{zz} - S_{nn} \).

From Eq. 6-116 and Eq. 6-117: \( S_{\theta \theta} = S_{nn} \).

By combining Eq. 6-115 to Eq. 6-117, the system can be reduced to two differential equations:

\[ \frac{DS}{Dt'} = a \left( S_{kk} + S - \frac{S}{D_{e,x}} - 2S_{zz} \right) + \frac{1-a}{2} \left( S_{kk} + S_{kk} S - 3D_{e,x} S - 2S_{zz} \right) \]  \hfill (6-118)

\[ \frac{DS_{kk}}{Dt'} = a \left( 2S\left(1 - \frac{S_{kk}}{L^2}\right) - \frac{S_{kk} - 3}{D_{e,x}} \right) \]  \hfill (6-119)

where \( S = S_{zz} - S_{nn} \) and \( S_{kk} = \text{tr} S \). The initial condition is: \( a(t') = 0 \), \( S_{kk} = 3 \) and \( S = 0 \).

The viscosity of the solution is found using Eq. 6-55. We have:

\[ \tau_{zz} = 2\eta_x E_{zz} - \nu kT L S_{zz} \]  \hfill (6-120)
and

\[ \tau_\pi = 2\eta_s E_\pi - \nu k T \lambda S_\pi \]  \hspace{1cm} (6-121)

Subtracting Eq. 6-121 from Eq. 6-120 gives:

\[ \tau_{zz} - \tau_\pi = 2\eta_s (E_{zz} - E_\pi) - \nu k T \lambda \frac{\partial}{\partial t'} \left( \frac{DS}{Dt'} - S_{kk} - S \right) \]  \hspace{1cm} (6-122)

Substituting \( E_{zz} - E_\pi = \frac{3}{2} \dot{\varepsilon} \) into Eq. 6-122 and rearranging gives:

\[ \frac{\tau_{zz} - \tau_\pi}{\dot{\varepsilon}} = 3\eta_s + \nu k T \lambda \left( S_{kk} + S - \frac{DS}{Dt'} \right) = \eta \]  \hspace{1cm} (6-123)
Combining Eq. 6-113 and Eq. 6-123 gives the following:

\[
\frac{\bar{\eta} - 3\eta_{s}}{3(\eta_{o} - \eta_{s})} = \frac{1}{3} \left( S_{kk} + \frac{S}{D} \frac{DS}{Dt} \right)
\] (6-124)

Results from Eq. 6-124 are shown in Fig. 6.13. It represents the normalized extensional viscosity of the solution as a function of \(D_{e_{ext}}\) for a value of \(L=100\). It shows the same tendencies as those described from the results of FENE-P: first a Newtonian behavior at low \(D_{e_{ext}}\) and then a sudden increase at certain critical \(D_{e_{ext}}\). As it would be expected from this, the same behavior is obtained for the relative elongation of the dumbbells \(<R^{2}/R_{0}^{2}>\) (or \(tS/L^{2}\) in dimensionless variables).

It is interesting to explore what role the parameter \(\alpha\) plays in these results. Indeed, the results shown in Fig. 6.13 are independent of \(\alpha\). Figure 6.13 shows the maximum viscosity for each \(D_{e_{ext}}\) (the steady-state extensional viscosity). However, \(\alpha\) affects dumbbell extension at a given spatial position, since as time goes by, the dumbbells move and stretch simultaneously. Therefore, we can determine how long it takes for a dumbbell to achieve a specific size and also the location at which this first happens. Consider a strand whose dimensionless thickness is \(h\), such that it is there where the dumbbells first reach half of its maximum length \(L\). This means: \(h = 2r_{1/2} = L/2\) (see Fig. 6.14). The time at which this state is reached changes with \(\alpha\), is shown in Fig. 6.15 where the dimensionless thickness of this strand is presented as function of \(D_{e_{ext}}\). Figure 6.15 shows that as \(D_{e_{ext}}\) increases, \(h\) increases and then approaches a specific value asymptotically. Such value depends on \(\alpha\).
Within the strand, the dumbbell length increases from $L/2$ at the outer edge of the strand to higher values as the axis of symmetry is approached.

Figure 6.14. Strand of dimensionless thickness $h$ in which the dumbbells are stretched beyond $L/2$.

$$h = 2r_{|s=L/2}$$

Figure 6.15. Dimensionless thickness of the strand ($h$) as a function of $De_{ax}$. Calculated with Lhuillier's dumbbell model for different values of $a$. 
Figure 6.16 shows the dimensionless time required for the dumbbells to stretch to a size $L/2$ as a function of $De_{ext}$ for different values of $a$. Consistently, as $De_{ext}$ increases, less time is necessary to stretch the dumbbells. Also, for a fixed $De_{ext}$, as $a$ decreases, the dumbbells need more time to become stretched. This supports the fact that $a$ is related to the ability of the flow to stretch the molecules at certain strain rate.

![Figure 6.16. Dimensionless time for the dumbbell to reach a length $L/2$ as a function of $De_{ext}$. Calculated with Lhuillier's dumbbell model for different values of $a$.](image)

Comparing the models under discussion, Fig. 6.17 shows the relative dumbbell elongation for uniaxial extensional flow for the evolution equation with finite extensibility, the FENE-P model and Lhuillier’s model for a value of $L=100$. The curves practically collapse in one, and this result has several implications: (1) neglecting Brownian motion in the evolution equation of a single dumbbell seems not to have a large effect on the response of the system. We should keep in mind that Langevin’s
equation follows a single dumbbell whereas the other two models consider a distribution of dumbbells; (2) the hydrodynamic interactions considered in Lhuillier's model do not show an effect that is critical in the evolution of the dumbbell elongation. In the following section, hydrodynamic interactions will be accounted for by introducing a variable friction coefficient in the FENE-P dumbbell.

![Graph showing relative dumbbell elongation](image)

**Figure 6.17.** Relative dumbbell elongation in uniaxial extensional flow as a function of $D_{ext}$. Comparison between Langevin's equation (including finite extensibility), FENE-P dumbbell model and Lhuillier's dumbbell model. The maximum dimensionless length of the dumbbell is $L=100$.

### 6.5.4. FENE-P Dumbbell Model with Hydrodynamic Interactions

In this section, the FENE-P dumbbell will be used in shear flow and extensional flow as was done before. The only difference is that the friction coefficient $\zeta$ will not be considered constant, but it will be considered a linear function of the end-to-end distance of the dumbbell. The friction law was proposed by Hinch and de Gennes (Eq. 6-63).
When we introduce a variable friction coefficient, it is not possible to obtain a constitutive equation of the type of Eq. 6-59 since the terms involving the relaxation time $\lambda$ will be multiplied by $\sqrt{\frac{1}{3} \text{tr} S}$. An assumption to be made at this point is that for the new friction coefficient, the Peterlin approximation is also valid. That is, it is still possible to use the continuity equation (Eq. 6-22) to obtain an expression for $\langle RR \rangle$. The same was done by other researchers (97) to keep the simplicity of the model. The starting point will be Eq. 6-32, where $F^C$ is given by Eq. 6-43 and $\zeta$ is given by Eq. 6-63. With these modifications and using the same dimensionless variables used before, one obtains:

$$\left( \lambda \sqrt{\frac{1}{3} \text{tr} S} \right) \mathbf{S} = -\frac{1}{1 - \frac{\text{tr} S}{L^2}} \mathbf{S} - \mathbf{I} \quad (6-125)$$

and the expression for the stress tensor is given by Eq. 6-55.

6.5.4.1 Steady Uniaxial Extensional Flow

The following system of differential equations results from Eq. 6-125:

$$De \sqrt{\frac{1}{3} S_{kk}} \left( \frac{DS_{xz}}{Dt} - 2S_{xz} \right) = -\frac{1}{1 - \frac{S_{kk}}{L^2}} S_{xz} + \mathbf{I} \quad (6-126)$$

$$De \sqrt{\frac{1}{3} S_{kk}} \left( \frac{DS_{xx}}{Dt} + S_{xx} \right) = -\frac{1}{1 - \frac{S_{kk}}{L^2}} S_{xx} + \mathbf{I} \quad (6-127)$$
Figure 6.18. Relative dumbbell elongation in uniaxial extensional flow as a function of $De_{ext}$. Calculated with FENE-P dumbbell model considering non-constant friction coefficient. The maximum dimensionless length of the dumbbell is $L=100$.

$$De_{ext} \sqrt{\frac{1}{3} S_{kk} \left( \frac{DS_{\theta\theta}}{Dt'} + S_{\theta\theta} \right)} = \frac{1}{1 - \frac{S_{kk}}{L^2}} S_{\theta\theta} + 1 \quad (6-128)$$

From Eq. 6-127 and Eq. 6-128: $S_{\theta\theta} = S_{\pi}$.

Combining Eq. 6-126 to Eq. 6-128, the system to be solved can be reduced to two differential equations:

$$\frac{DS}{Dt'} - S - S_{kk} = -\frac{1}{De_{ext} \sqrt{\frac{1}{3} S_{kk} \left( 1 - \frac{S_{kk}}{L^2} \right)}} S \quad (6-129)$$

and
\[
\frac{DS_{kk}}{Dt'} - 2S = -\frac{1}{De_{\text{ext}}} \left( \frac{1}{3} S_{kk} \right) \left( \frac{1}{1 - S_{kk}/L^2} \right) - 3 \]  
(6-130)

where \( S = S_{kk} - S_c \) and \( S_{kk} = \text{tr} \ S \). The initial condition is: \( t' = 0, \ S_{kk} = 3 \) and \( S = 0 \).

The expression for calculating the normalized viscosity of the solution is Eq. 6-124.

Figure 6.18 shows a plot of \( S_{kk}/L^2 \) as a function of \( De_{\text{ext}} \) when \( L = 100 \). The results show that for a range of \( De_{\text{ext}} \) between approximately 0.02 up to 0.3, there is more than one possible solution. If we start at low \( De_{\text{ext}} \) with the molecule in the coiled state, a strong flow is needed to stretch the undeformed random coil until a critical \( De_{\text{ext}}^{C-S} \) value is reached. Figure 6.19 shows that this value is the equivalent for both situations: constant and non-constant friction. These two approaches are also indistinguishable when \( De_{\text{ext}} \) is lower than \( De_{\text{ext}}^{C-S} \). The molecules undergo coil-stretch transition instantaneously for the case of non-constant friction coefficient, whereas it occurs progressively when the friction coefficient is constant. The increasing solvent-molecule friction is responsible for this steeper change. As more segments of the chain are exposed to the solvent, it will be easier to stretch the molecules due to the enhanced 'grip' by the solvent. Once extended (at a \( De_{\text{ext}} \) greater than \( De_{\text{ext}}^{C-S} \)), the molecules can be maintained like that by a much reduced flow strength because of the increased friction with the solvent. Thus, when decreasing \( De_{\text{ext}} \) starting from a value beyond \( De_{\text{ext}}^{C-S} \), it is necessary reach a value that is below \( De_{\text{ext}}^{S-C} \) in order to obtain a coiled conformation again (see Fig. 6.18). Therefore, the transitions between coiled and stretched states have hysteresis.
Figure 6.19. Relative dumbbell elongation in uniaxial extensional flow as a function of $De_{ext}$. Calculated with FENE-P dumbbell model considering both, constant and non-constant friction coefficient. The maximum dimensionless length of the dumbbell is $L=100$.

6.5.4.2 Steady Shear Flow

A set of algebraic equations from Eq. 6-125 is obtained:

\[ 2 \left( \frac{De_{shear}}{S_{kk}} \right) S_{xx} = \frac{1}{1 - \frac{S_{kk}}{L^2}} S_{xx} - 1 \]  \hspace{1cm} (6-131)

\[ 0 = \frac{1}{1 - \frac{S_{kk}}{L^2}} S_{yy} - 1 \]  \hspace{1cm} (6-132)
Equations 6-131 to 6-134 are solved and then the normalized viscosity of the solution can be calculated using Eq. 6-114. Figure 6.20 shows curves of the normalized viscosity considering constant and non-constant friction coefficient for $L^2=1000$. Once the onset for the shear thinning of the solution is reached, the criticality of the phenomenon increases. This behavior is analogous to that observed in uniaxial extension (Fig. 6.19).
The onset of shear-thinning is associated with the change in conformation of the dumbbells. Such changes occur more easily as the number of segments exposed to the solvent increases when considering non-constant friction coefficient, and this is reflected in the behavior of the viscosity, which decreases more dramatically with $D_{e,\text{shear}}$ when the friction coefficient varies.

In the following section, experimental data obtained in a viscometer (shear flow) and with the opposed jets system (uniaxial extensional flow) will be used to obtain information based on theoretical arguments as to how the polymer/surfactant interactions might proceed as well as to predict structural changes in the polymer chains once these interactions are present.

**6.6. Complex Formation between Polymer and Surfactant**

Part of a recent study (98) on complex formation between a semiflexible nonionic polymer, hydroxypropylcellulose (HPC) and a cationic surfactant, hexadecyltrimethylammonium bromide (HTAB) consists on determining the contribution of micellar aggregates to the solution viscosity based on concepts developed for dilute polymer solutions. Their experiments agree with previous observations where the viscosity of polymer/surfactant solutions increases as surfactant concentration increases beyond the CAC until it reaches a maximum at the PSP (38).

The viscosity of the solution is expressed as a combination of several contributions:

$$
\bar{\eta} = \eta_s + \eta_a + \eta_{\text{surf}} + \eta_f
$$

(6-135)
where $\eta_{\text{surf}}$ is the excess viscosity due to surfactant alone in water, and $\eta_i$ is the excess viscosity due to the interactions between polymer and surfactant. Notice that this equation is equivalent to Eq. 6-81 with new terms due to the presence of a third component in solution. The decomposition expressed by Eq. 6-135 is expected to hold if all components are present in dilute concentration.

Using Eq. 6-135 $\eta_i$ was calculated from experimental data on $\bar{\eta}$ and then $\eta_i / \eta_{1,\text{PSP}}$ was plotted as a function of [HTAB]/[HPC] (concentration of surfactant/concentration of polymer) for all HPC concentrations used. In this case, the CAC is almost zero, thus it is assumed that CAC=0; the parameter $\eta_{1,\text{PSP}}$ is the viscosity due to the polymer-surfactant interactions at the PSP. The result was a unique curve which indicates that for a given number of surfactant micelles bound per chain (i.e., a constant [HTAB]/[HPC]), the ratio of the interaction viscosity relative to its value at maximum binding ($\eta_i / \eta_{1,\text{PSP}}$) is the same regardless of the polymer concentration. Such behavior was also observed in the presence of NaCl (98). The origin of such scaling is not clear, but it is explained in terms of dilute solution regime arguments. Using Einstein's law, the polymer contribution to viscosity is:

$$\eta_r = \eta_i (2.5vL_{\text{hp}}) \quad (6-136)$$

where $L_{\text{hp}}$ is the hydrodynamic volume of a polymer chain and $v$ is the number of polymer molecules per unit volume. Using similar expressions for the surfactant and the complex (micellar aggregates+polymer) and neglecting the contribution of the surfactant ($\eta_{\text{surf}}$), one obtains (98):
\[
\frac{\eta_1}{\eta_{1,\text{PSP}}} = \frac{n_c}{n} \left( \frac{V_{hc} - V_{hp}}{V_{hc}^\text{max} - V_{hp}} \right)
\]

(6-137)

where \( n_c \) is the number concentration of complexed polymer such that \( n = n_c + n_p \), and \( n_p \) is the concentration of free polymer. \( V_{hc} \) is the hydrodynamic volume of the complex, and \( V_{hc}^\text{max} \) is the value of \( V_{hc} \) at maximum binding (PSP). The fraction of chains that form the complex \( (n_c/n) \) and the degree of swelling of the complex hydrodynamic volume, \((V_{hc} - V_{hp})/(V_{hc}^\text{max} - V_{hp})\), both depend on the ratio \([\text{HTAB}]/[\text{HPC}]\) exclusively.

For the case of HTAB, the value of the CAC is very close to the value of the CMC, and both are close to zero. This means that the ratio \([\text{HTAB}]/[\text{HPC}]\) is equivalent to \([\text{HTAB}]_{\text{complexed}}/[\text{HPC}]\), because from the start (low \([\text{HTAB}]\)), the surfactant is forming aggregates along the polymer chains. Also, no matter what aggregation model one chooses for the surfactant, the PSP tends to the same value at low polymer concentrations.

To follow an equivalent analysis for the PEO/SDS system, first we need to find a dependence of \( n_c/n \) on the surfactant added to the system. Following the same approach explained above, we postulate that \( \frac{n}{n} \propto \frac{[\text{SDS}]_{\text{complexed}}}{[\text{PEO}]} \). Now, we try to find theoretical arguments to specify this dependence.

Simple aggregation models must be proposed in order to determine \([\text{SDS}]_{\text{complexed}}\), since it is not clear how aggregation proceeds at the molecular level. Some researchers
(42,99) maintain that as aggregation proceeds, the polymer chains saturate with micellar aggregates, and further addition of surfactant results in a partitioning between the aggregates (increasing their aggregation number) and the bulk solution. This means that the polymer chain saturates with surfactant only when the bulk concentration of surfactant reaches the CMC. Further surfactant addition beyond the PSP results in free micelle formation. Other researchers (1.33) report that after the PSP is reached, all the surfactant added dissolves as monomer in the bulk until the CMC is reached, meaning there is a gap of surfactant concentration between the PSP and free micelle formation. More recently, it has been reported (100) that free micelles and aggregates form simultaneously, so free micelles may occur below the PSP. We explore two extreme cases. The first model (Model 1) assumes that during surfactant aggregation the polymer chains are either free or saturated of micellar aggregates (i.e. the amount of polymer complexed varies linearly with SDS concentration between the CAC and the PSP). The second model (Model 2) considers that as micellar aggregation proceeds, the number of micellar aggregates along all the PEO chains is the same. Both models assume that beyond the CAC and until the PSP is reached, all the SDS added is forming micellar aggregates along the PEO chains.

6.6.1. Model 1: Progressive Saturation of PEO chains

This model assumes that $n_n$ varies with [SDS] as:

$$n_n = 0 \quad [\text{SDS}] < \text{CAC}$$  (6-138)
\[ n_c = \frac{\nu}{PSP - CAC}, \quad \text{CAC} < [SDS] < PSP \quad (6-139) \]

\[ n_c = \nu \quad \text{[SDS]} > \text{PSP} \quad (6-140) \]

Figure 6.21 illustrates this model.

Equation 6-139 indicates that \( n_c \) varies linearly with [SDS] in the range between the CAC and the PSP. Therefore, throughout the binding process, we have both free and saturated polymer chains. This model does not consider the fact that the probability for an aggregate to form on a specific site on the polymer chain depends on the number of aggregates in its proximities, and also on the probability of having some sites along the polymer chains that are more likely than others to admit an aggregate due to steric hindrances. In addition to this, these considerations involve continuous change as micellar aggregates form.

It is also necessary to propose a model for describing the changes in the amount of surfactant forming micellar aggregates, with respect to the total amount of added...
surfactant. Figures 6.22 and 6.23 show some alternatives:

![Graph showing examples of aggregation of SDS as a function of [SDS].]

Figure 6.22. Examples of aggregation of SDS as a function of [SDS].

![Graph showing change of [SDS]_free as a function of [SDS].]

Figure 6.23. Change of [SDS]_free as a function of [SDS].

Three different examples of surfactant aggregation are considered. Figure 6.22 shows that in case A, the surfactant aggregates linearly, starting from the CAC until the amount of surfactant bound to the polymer chains is equal to PSP-CAC. Thus, we are considering that every molecule of surfactant that is added to the system beyond the CAC is binding to the polymer. The evolution of the amount of free surfactant in solution is shown in Fig.
6.23. Once the total concentration of surfactant is equal to the CAC, the concentration of free surfactant remains equal to the CAC until the PSP is reached. Notice that case A is not consistent with a situation in which free micelles form in solution once the total concentration of surfactant is the PSP. Thus, if the concentration of polymer in solution is close to 0, then PSP→CAC. Cases B and C are less simple. Figure 6.22 shows that case B consists on total aggregation of the added surfactant up to an intermediate point where it begins partitioning between the bulk solution and micellar aggregates until the PSP is reached. Case C on the other hand, considers that partitioning starts at the CAC. Figure 6.23 shows that the amount of free surfactant in case B follows the same path as case A up to an intermediate concentration where it starts increasing, whereas for case C, such increase occurs throughout the whole range between the CAC and the PSP. Notice that these two aggregation models are consistent with formation of micelles in solution once the total surfactant concentration is the PSP.

Let us assume that the surfactant aggregation follows case A. This is defined as:

\[ [\text{SDS}]_{\text{free}} = 0. \quad [\text{SDS}] < \text{CAC} \quad (6-141) \]

\[ [\text{SDS}]_{\text{free}} = [\text{SDS}] - \text{CAC} \quad \text{CAC} < [\text{SDS}] < \text{PSP} \quad (6-142) \]

It has been determined that the PSP of SDS varies approximately linearly with PEO concentration \([\text{PEO}]\) \((1.31)\). Therefore, for case A we have:

\[ \text{PSP} - \text{CAC} \propto [\text{PEO}] \quad (6-143) \]

Substitution of Eq. 6-143 into Eq. 6-139 gives:
Figure 6.24. Zero shear viscosity of PEO/SDS solutions in 0.1 M NaCl as a function of SDS concentration. The average molecular weight of the polymer ($\overline{M}_w$) is $6\times10^5$. Values in the legend represent PEO concentrations (2).

\[
\frac{\eta}{\nu} \propto \frac{[\text{SDS}] - \text{CAC}}{[\text{PEO}]} = \frac{[\text{SDS}]_{\text{complexed}}}{[\text{PEO}]} \quad \text{CAC} < [\text{SDS}] < \text{PSP} \quad (6-144)
\]

This expression is similar to that used by Hormnirun et al. (98) in their work, and the interest is to explore if the scaling that works for the HTAB/HPC system also applies to our system. It is important to mention that this scaling is valid even when the surfactant concentration is higher than the PSP. In our case, we tried to justify their approximation with an aggregation model that results in Eq. 6-144, but that is valid only up to the PSP.

We will apply Eq. 6-144 as they do with their results to explore the behavior, but being aware of no further justification for $[\text{SDS}] > \text{PSP}$. Then we will consider that the surfactant is 'complexing' with the polymer by promoting the electrostatic screening of
To begin, we start with results of shear viscosity obtained by Garcés (2) with PEO of two average molecular weights (\(\overline{M}_w = 6 \times 10^5\) and \(\overline{M}_w = 8 \times 10^6\)) and SDS. Next, we will use the results from the opposed jets with the PEO of \(\overline{M}_w = 4 \times 10^6\) and SDS.

Figures 6.24 to 6.26 show the results of shear viscosity as a function of [SDS], for \(\overline{M}_w = 6 \times 10^5\) and \(\overline{M}_w = 8 \times 10^6\), changing [PEO], as well as in the absence and presence of NaCl. Notice that for the lower \(\overline{M}_w\) (Fig. 6.24), the viscosity decreases in the presence of SDS and salt. This result evidences that NaCl is promoting coil contraction, so that the polymer/surfactant complex contribution to the viscosity of the solution decreases with...
polymer concentration.

Figure 6.26. Zero shear viscosity of PEO/SDS solutions as a function of SDS concentration at $[\text{PEO}]=100$ ppm ($\bar{M}_w = 8 \times 10^6$) in the absence and in the presence of 0.1 M NaCl (2).

For the high molecular weight polymer, Figs 6.25 and 6.26 show for 50 and 100 ppm PEO ($\bar{M}_w = 8 \times 10^6$) respectively, that at low surfactant concentrations in the presence of salt, the viscosity remains constant and lower than for solutions where salt is not present. Then, at a specific concentration, it starts increasing more rapidly with surfactant concentration than it does in the absence of salt. This result is consistent with the observations in Chapter II. The surfactant concentration at which the maximum viscosity occurs corresponds to the PSP. At low SDS concentrations, the micellar aggregates can interact with two or more different portions of the polymer coil, favoring intramolecular interactions. Then, as more aggregates form, intramolecular interactions are more
difficult and now, intermolecular interactions gain importance to a point where these are stronger than in the absence of salt. Figures 6-27 to 6-29 show results of $\eta_I / \eta_{I,PSP}$ as a function of ([SDS]-CAC)/[PEO] for the shear viscosity data shown in Figs. 6-24 to 6-26. The CAC and PSP values used in the calculations are shown in Table D.1 (Appendix D).

Figure 6.27 shows the result of the scaling for the solutions with PEO of $M_w=6\times10^5$ in the presence of NaCl. In this case, the PSP was taken to be the concentration at the minimum in the viscosity curves (Fig. 6.24). The results show that there is actually a relatively good scaling of the data, for which the model proposed seems to give a good description of what the aggregation mechanism could be.

![Normalized interaction viscosity of PEO/SDS solutions in 0.1 M NaCl as a function of the ratio of SDS complexed and PEO ($M_w=6\times10^5$). Values in the legend represent PEO concentrations.](image-url)
Figures 6.28 and 6.29 show the results obtained for the solutions of PEO of molecular weight $8 \times 10^6$ in the presence and absence of NaCl respectively. It is evident that these data are far from fitting the proposed model. More results from application of this model are shown in Appendix D. In order to explore a possible aggregation model, the results of these figures were "forced" to match into a master curve that corresponded to a PEO concentration of 50 ppm. From here, we could obtain curves for $n_c$ as a function of [SDS] that allow us to obtain a unique curve of $\eta_l / \eta_{l,PSP}$ vs. $n_c / \nu$. Figures 6.30 and 6.31 show these results. The aggregation curves for 25 and 100 ppm PEO solutions look quite different from the linear aggregation we have been considering. For the case with
no NaCl in solution (Fig. 6.30), it seems that when [PEO] is 100 ppm, there is a more even distribution of SDS throughout the polymer chains, instead of a progressive chain saturation. This occurs as soon as aggregation starts, and then the process slows down for a certain [SDS] range. Until further increase in aggregation occurs until the PSP is reached. Obviously, this is still assuming a model where there are free chains present in solution before saturation. For 25 ppm, on the other hand, the process agrees with a model that considers partition of the surfactant between the polymer and the solution phase. For solutions in the presence of salt, Fig. 6.31 shows an aggregation pattern for 100 ppm PEO similar to that observed in Fig. 6.30.

Figure 6.29 Normalized interaction viscosity of PEO/SDS solutions as a function of the ratio of SDS complexed and PEO ($\bar{M}_w = 8 \times 10^6$). Values in the legend represent PEO concentrations.
Figure 6.30. Concentration of complexed PEO \( n_e \) as a function of total SDS concentration (for PEO\( M_w =8\times10^5 \)). Values of \( n_e \) are values such that will allow for obtaining a master curve of normalized interaction viscosity. Values in the legend represent PEO concentrations. Dashed lines represent original \( n_e \) values calculated from data.

An equivalent analysis was performed with the results obtained with the opposed jets. No viscosity data are available for the solutions used in the opposed jets. Let us propose that the viscosity of these solutions was proportional to the inverse of the critical strain rate for network formation, i.e. \( \eta \propto \frac{1}{\dot{\epsilon}_n} \). As explained before, the value of \( \dot{\epsilon}_n \) corresponds to the onset of extension thickening, which is an indication of an increase in the apparent viscosity of the solution. Neglecting the contribution of free surfactant we can state.
Figure 6.31. Concentration of complexed PEO ($n_c$) as a function of total SDS concentration in 0.1 M NaCl solutions (for PEO: $M_{w} = 8 \times 10^6$). Values of $n_c$ are values such that will allow for obtaining a master curve of normalized interaction viscosity. Values in the legend represent PEO concentrations. Dashed lines represent original $n_c$ values calculated from data.

$$
\eta_t = \frac{1}{\varepsilon_{n+1 \text{PEO-SDS}}} - \frac{1}{\varepsilon_{n+1 \text{PEO}}} \tag{6-145}
$$

and then

$$
\frac{\eta_t}{\eta_t \text{ PSP}} = \frac{1}{\varepsilon_{n+1 \text{PEO-SDS}} \dot{\varepsilon}_{n+1 \text{PEO}}} - \frac{1}{\dot{\varepsilon}_{n+1 \text{PEO}}} \tag{6-146}
$$

Two limitations of this approximation are: (1) no calculation can be done on solutions where no transient network formation is present; (2) for concentrations of polymer that fall close to the dilute regime, our system gives accurate enough information regarding
PSP values, since at a certain [SDS] no further displacements of $\varepsilon_*$ are observed; however, as the concentration of polymer increases, the values of $\varepsilon_*$ get to be too low to be measured with accuracy. For these two reasons, we are limited to manipulate data within a specific range of polymer concentrations, so we need polymer concentrations for which changes between the CAC and the PSP can be detected with our set up. Comparison with literature results on the PSP was made to ensure appropriate choices.

Figure 6.32. Normalized interaction viscosity of PEO/SDS solutions as a function of the ratio of SDS complexed and PEO ($\bar{M}_w =4\times10^5$) using experimental data obtained with jets I (see section 4.2). Values in the legend represent PEO concentrations.

Figure 6.32 shows a plot of $\eta_I/\eta_{I,\text{PSP}}$ vs. $n_z/\nu$ for three different PEO concentrations. The data collapse to a single curve. Therefore, even though the aggregation model could be different, we might be able to predict values of $\varepsilon_*$ for
PEO/SDS solutions by knowing $\phi_n$ for the pure polymer solution and for solutions where $[SDS]=\text{PSP}$.

6.6.2. Model 2: Progressive Aggregation of SDS to PEO chains

A second aggregation model is proposed to allow for the calculation of geometric parameters of the polymer coils. In order to do this, it is necessary to use a model for which the coil conformation is the same for all polymer chains. This means that if we have a polymer chain with one bound aggregate, then the rest of the chains must have one aggregate as well, and so on. Figure 6.33 illustrates the model proposed.

Notice that aggregation starts, there is not enough surfactant to form at least one aggregate in each polymer chain. From there the assumption of same conformation for all polymer chains is valid only beyond a surfactant concentration $S'$. However, an estimate of $S'$ results in a value very close to the CAC. For example, if we say that 1 aggregate contains 60 surfactant molecules, it is necessary to add 0.015 mM of SDS beyond the

![Figure 6.33: Amount of polymer complexed as a function of [SDS] (Model 2).](image-url)
CAC to have one aggregate per chain in a 1000 ppm PEO solution of \( M_w = 4 \times 10^6 \).

Therefore, we can say that the model is valid for the whole range CAC to PSP (S' is very close to the CAC).

A radius of gyration can be calculated as a function of number of surfactant molecules (or number of micellar aggregates) per polymer chain. The first step is to calculate the intrinsic viscosity, defined as:

\[
[\eta] = \left( \frac{\eta_{sp}}{C_p} \right)_{C_p \to 0}
\]

(6-147)

where \( C_p \) is the polymer concentration and \( \eta_{sp} \) is the specific viscosity. The specific viscosity is:

\[
\eta_{sp} = \frac{\eta - \eta_s}{\eta_s}
\]

(6-148)

The intrinsic viscosity is found by extrapolating the data of \( \frac{\eta_{sp}}{C_p} \) from dilute solutions to find the corresponding value at zero polymer concentration. Then, using a structural model, we can relate \([\eta]\) to the dimensions of the coil. If we start from Eq. 6-113 (zero-shear viscosity from Lhuillier's model), we realize that the geometrical features of the coil are included in the parameter \( \lambda \). From Eq. 6-35, we see that this dependence relies on \( \beta^* \) and \( \zeta^* \). Combining Eq. 6-1, Eq. 6-3 and Eq. 6-5, one obtains:

\[
\beta^* = \frac{1}{4R_s^*}
\]

(6-149)
The radius of the beads $r_0$ is equivalent to the radius of the coil, which at the same time is proportional to the most probable radius of gyration of the coil at equilibrium. From this, we get: $\zeta \approx 6\pi r_0 R_g$. Plugging Eq. 6-149 into Eq. 6-35, and the definition of $\zeta$ gives:

$$\frac{1}{\eta_0} - \frac{1}{\eta_s} = \nu kT \frac{6\pi \eta_s R_g}{8kT \left( \frac{1}{4R_g^2} \right)}$$

(6-150)

Since $R_g$ in Eq. 6-150 is calculated in equilibrium conditions (zero-shear), it will be called $R_g^{eq}$. Rearranging Eq. 6-150 yields:

$$\eta_s = \frac{\eta_0 - \eta_s}{\eta_s} = 3\pi \nu R_g^{eq}$$

(6-151)

In terms of polymer concentration $R_g^{eq}$ is obtained from Eq. 6-151:

$$R_g^{eq} (nm) = 5.6067 \left( \frac{M_w (g/mol) \left( \frac{\eta_s}{C_p (ppm)} \right)}{C_p (ppm)} \right)^{1/3}$$

(6-152)

The number of surfactant molecules per unit chain ($N_v$) is calculated as:

$$N_v = \frac{[Surfactant]_{complexed} (mM)}{C_p (ppm)}$$

(6-153)

In order to make calculations simpler, case $A$ will be considered as the model for surfactant aggregation (linear aggregation).
The radius of gyration was calculated for the HPC/HTAB system using Eq. 6-152. Since we are using many approximations, the absolute values of our calculations are not expected to represent real values, but will provide important information as to how the coil dimensions change in the presence of surfactant with respect to a reference value. The reference value taken is the $R_{g, eq}$ calculated for pure PEO. Then, ratios of the values obtained are calculated to determine by how much $R_{g, eq}$ has changed. Figure 6.34 shows the ratio $R_{g, eq}/R_{g, eq0}$ as a function of $N_s$, where $R_{g, eq0}$ is the equilibrium radius of gyration of the pure polymer. The radius of gyration decreases before the PSP is reached, and from there, it starts increasing. This is the opposite of what we would expect by looking at the experimental data, where the viscosity increases for HTAB concentrations below...
the PSP. It is important to mention that Eq. 6-152 is applicable to flexible polymer chains, and HPC is a semiflexible polymer, and this could be one reason why the results are not in agreement with what is expected. Calculated [η] values for each polymer and surfactant concentration do not reproduce the original viscosity data, which means that it is not right to assume that the system is in the dilute solution regime as mentioned by the authors. For this reason, the partial theoretical justification offered in Hormnirun et al. (98) based on Einstein's law should not be valid.

\[ R_{g,eq}/R_{g,eq0} \]

![Graph](image)

Figure 6.35 Relative change in polymer radius of gyration as a function of the number of surfactant molecules per polymer chain for PEO/SDS solutions in 0.1 M NaCl (for PEO: $\bar{M}_w = 10^5$). Data from shear flow experiments (2).

The same analysis was done for the PEO/SDS system with both shear and extensional flow data. The results obtained with shear are shown in Fig. 6.35 and Fig. 6.36. Here, $R_{g,eq}/R_{g,eq0}$ vs. $N_s$ is shown for PEO with $\bar{M}_w = 6 \times 10^5$ and $\bar{M}_w = 8 \times 10^6$ respectively.
Figure 6.35 shows that in the presence of NaCl, there is a continuous decrease in \( \frac{R_{g,eq}}{R_{g,eq0}} \) as \( N_r \) increases. This is an evidence of a contraction of the coil with respect to the situation where the polymer is pure in solution. The low value of \( \overline{M}_w \) seems to be responsible for the lack of intermolecular interactions. Here, intramolecular interactions dominate over intermolecular interactions. On the other hand, the behavior is opposite for the higher molecular weight, as shown in Fig. 6.36. This means that we can expect an aggregation pattern in the presence of NaCl that changes when the molecular weight of the polymer is very high. Figure 6.36 also allows for comparison with the evolution of \( \frac{R_{g,eq}}{R_{g,eq0}} \) in the absence of NaCl.

![Figure 6.36. Relative change in polymer radius of gyration as a function of the number of surfactant molecules per polymer chain for PEO/SDS solutions in the absence and in the presence of 0.1 M NaCl (for PEO. \( \overline{M}_w = 8 \times 10^5 \)). Data from shear flow experiments (2).](image-url)
In the case of extensional flow, again we face the problem of not having absolute
values of viscosity defined. For this reason, we still consider the assumption stated above,
\[ \bar{\eta} \propto \frac{1}{\dot{\varepsilon}_n} \]. To obtain values of \( R_{g,eq} \), it is necessary to have data on \( \eta_{sp} \). To estimate reasonable values of this parameter, we need to estimate values for the viscosity of the solutions. We can start by saying that the proportionality between \( \bar{\eta} \) and \( \dot{\varepsilon}_n \) is given by a constant \( A \):

\[ \bar{\eta}_{\eta,\eta_0} = \eta_0 = A \frac{1}{\dot{\varepsilon}_n} \quad (6-154) \]

Substitution of Eq. 6-154 into Eq. 6-151 gives:

\[ \eta_{sp} = \frac{A}{\eta_s \dot{\varepsilon}_n} - 1 \quad (6-155) \]

Now we need to estimate the order of magnitude of the proportionality constant \( A \). From Eq. 6-155 it is evident that the first term on the right hand side must be greater than 1, meaning that: \( A > \eta_s \dot{\varepsilon}_n \). The orders of magnitude of \( \eta_s \) (Pa s) and \( \dot{\varepsilon}_n \) (s\(^{-1}\)) are \( O(10^3) \) and \( O(10^5) \) respectively. We conclude then that \( A > O(1) \). Let us assign arbitrarily \( A = 10 \). Thus, we have:

\[ \eta_{sp} \approx \frac{10^2 \left[ \frac{1}{\dot{\varepsilon}_n} \right] - 1}{[\text{PEO}]} \quad (6-156) \]

Equation 6-156 will be used to estimate values that allow for a calculation of \([\eta]\) and in consequence \( R_{g,eq} \). Figure 6.37 shows the ratio \( R_{g,eq} / R_{g,eq0} \) as a function of \( N \). When SDS
is added. $R_{g,eq}$ increases dramatically with respect to the pure polymer. The ratio reaches a value of almost 5, which in terms of volume occupied by the coils is a large change. Therefore, intermolecular interactions are strongly promoted by this increase in size. From the calculated values of $[\eta]$, we obtain that $c^*$ is reduced close to two orders of magnitude when the polymer chains are saturated with surfactant, compared to the pure polymer. This result is consistent to the changes in $c^*$ measured experimentally for the PEO/SDS system (58). On the other hand for the solutions where NaCl is present, $R_{g,eq}$ decreases slowly with the number of surfactant molecules present per polymer chain.

![Graph showing relative change in polymer radius of gyration as a function of the number of surfactant molecules per polymer chain for PEO/SDS solutions in the absence and in the presence of 0.1 M NaCl.](image)

Figure 6. Relative change in polymer radius of gyration as a function of the number of surfactant molecules per polymer chain for PEO/SDS solutions in the absence and in the presence of 0.1 M NaCl (for PEO $M_w = 4 \times 10^5$). Data from experiments with jets 1 (see section 4.2).
APPENDIX A

HYDRODYNAMICS OF OPPOSED-JETS FLOW

In this section, the expression for the strain rate used in Chapters II to V will be deduced. Then, the possible contributions to the pressure drops through the opposed jets will be studied using the mechanical energy balance. At the end, there will be a brief discussion on important aspects to consider when measuring the volumetric flow rate.

A.1. Definition of Strain Rate

The expression for calculating the strain rate in uniaxial extension is obtained as follows:

Consider an element of fluid along the axis \( r=0 \) at an arbitrary position \( z \) at time \( t \) as shown in Fig. A.1:

1. At \( t=t \)

![Figure A.1. Element of fluid passing through the opposed jets along \( r=0 \)](image)

In Fig. A.1 the following holds:
Since point $z$ is closer to the stagnation point, Eq. A-1 implies that the fluid element will stretch. At time $t=\Delta t$ the fluid element has deformed as follows:

2. At $t=t-\Delta t$

![Diagram showing deformation of the fluid element](image)

Figure A.2. Deformation of the fluid element in Fig. A.1 at time $t=t-\Delta t$

The deformation rate of the fluid element can be defined as:

\[
\begin{Bmatrix}
\text{Deformation} \\
\text{rate} \\
\text{of fluid element}
\end{Bmatrix} = \frac{\Delta l \Delta z}{\Delta t}
\]

(A-2)

where the length $\Delta l$ is given by: $\Delta l = (v_z|_{z-\Delta z} - v_z|_z)\Delta t$. Then, Eq. A-2 becomes:

\[
\begin{Bmatrix}
\text{Deformation} \\
\text{rate} \\
\text{of fluid element}
\end{Bmatrix} = \frac{v_z|_{z-\Delta z} - v_z|_z}{\Delta z}
\]

(A-3)

If we consider the deformation rate at a point, such that $\Delta z=0$, we finally obtain:

\[
\begin{Bmatrix}
\text{Deformation} \\
\text{rate} \\
\text{of fluid element}
\end{Bmatrix} = \dot{\varepsilon} = \lim_{\Delta z \to 0} \frac{v_z|_{z-\Delta z} - v_z|_z}{\Delta z} = \frac{\partial v_z}{\partial z}
\]

(A-4)

Using Eq. A-4, the strain rate for the opposed jets is given by:
\[ \dot{v} = \frac{v_z}{(\delta/2)} \]  \hspace{1cm} (A-5)

where \( v_z \) is the average velocity of the fluid inside one capillary, and \( \delta \) is the distance separating the capillaries. This velocity can be expressed in terms of the total volumetric flow rate as:

\[ v_z = \frac{Q \pi D^2}{2 \cdot 4} \]  \hspace{1cm} (A-6)

where \( D \) is the diameter of the capillary and \( Q \) is the total flow rate passing through both capillaries. Finally, after substituting Eq. A-6 into Eq. A-5, one obtains:

\[ \dot{v} = \frac{4Q}{\pi D^2 \delta} = \frac{Q}{A \delta} \]  \hspace{1cm} (A-7)

where \( A \) is the cross-sectional area of each capillary.

A.2. Estimate of pressure drop values using the mechanical energy balance

The mechanical energy balance will be used to estimate the pressure drop of water flowing through the opposed jets. Several sets of jets with differences in geometry are included in the analysis for comparison.

The dimensions of the different jets used in this analysis are shown in the following table:
Table A.1. Dimensions of the different opposed jets studied.

In order to determine whether the flow is laminar or turbulent inside the capillaries of the opposed jets shown in Table A.1, the necessary strain rate to achieve the critical Reynolds number (Re=2300) for transition from laminar to turbulent flow was calculated. Table A.2 shows these results:

Table A.2. Strain rate necessary for laminar-to-turbulent transition for the opposed jets studied.

The results in Table A.2 show that relatively high values of $\dot{\varepsilon}$ are needed to achieve...
turbulent flow with water. Only Jets 4 show a strain rate value considerably lower than
the rest. Thus, for our calculations, we can consider laminar flow for a fairly large range
of $\dot{e}$.

In order to apply the mechanical energy balance, the first step is to define the control
volume to be studied. Consider the test cell containing the opposed jets including the test
point for the second pressure transducer as the control volume. For this control volume
we have:

- It does not have any moving boundaries.
- No work is done on the control volume.
- Entrance effects from the fluid going into the cell are neglected.

Considering the former assumptions, the mechanical energy balance between the two
points where the pressure drop is measured yields:

$$
\left(\frac{1}{2g} v_1^2 + \frac{P_1}{\rho g} + z_1\right) - \left(\frac{1}{2g} v_2^2 + \frac{P_2}{\rho g} + z_2\right) = - \frac{E_v}{\rho g Q} \tag{A-8}
$$

where points 1 and 2 are the points with higher and lower pressure respectively, $E_v$ is the
rate of viscous dissipation to internal energy and $\rho$ is the density of the fluid. All the
viscous effects are lumped in $E_v$. This term divided by $\rho g Q$ is called the head loss. It
includes frictional head losses in straight sections of conduits, sudden expansions, etc.

Let's assume that the velocity in points 1 and 2 is approximately the same, and it is
also close to zero. Both points are considered to be at about the same height ($z_1 = z_2$).
Finally, Eq. A-7 simplifies to:
Equation A.9 predicts values of pressure drop through the jets ($\Delta P$) that only depend on the factors that contribute to the viscous dissipation. In this case, the following count: (a) losses due to uniaxial extension; (b) entry effects; (c) straight section of capillary; (d) expansion of the conduit (from the diameter of the capillary to the diameter of the glass tubing).

In order to calculate the losses due to uniaxial extension we need to start from the definition of $E_v$ (101):

$$
\dot{E}_v = \int \Phi dV
$$

where $\Phi$ is the rate of conversion to thermal energy per unit volume. The volume $V$ is where the uniaxial extension takes place. It is considered to occur in a cylindrical volume around the stagnation point given by $A\delta$. In cylindrical coordinates, $\Phi$ is defined as:

$$
\Phi = 2\eta_r \left( \frac{\partial v_r}{\partial r} \right)^2 + \left( \frac{v_r}{r} \right)^2 + \left( \frac{\partial v_z}{\partial z} \right)^2
$$

(A-11)

where $\eta_r$ is the fluid viscosity. For steady uniaxial extensional flow, in cylindrical coordinates, we have the velocity field: $v_z = \dot{\varepsilon} z$, $v_r = -1/2 \dot{\varepsilon} r$, $v_\theta = 0$. Substitution of this velocity field into Eq. A-11 and using Eq. A-10 one obtains:

$$
\left( E_v \right)_{\text{extension}} = 3\eta_r \dot{\varepsilon}^2 A\delta
$$

(A-12)

Combining Eq. A-12 and Eq. A-7, the head loss due to uniaxial extension is obtained:
Losses due to entry effects occur when the fluid enters the capillary. For a circular pipe, owing to the acceleration imparted to the fluid near the center of the pipe, the pressure drop in the entrance increases compared with that of a developed flow. The additional pressure drop at the entrance for laminar flow is (102):

\[ \Delta P = 1.16 \frac{\rho v^2}{2} \]  

Equation A.14 is valid for the distance from the entrance, whose magnitude is calculated as: \( z \eta \cdot \rho R^2 v_e = 0.115 \) (102). Here, \( R \) is the capillary radius. Calculation of \( z \) values for the different strain rates give entrance lengths of the order of the length of the straight sections.

Equation A.14 can be written in terms of \( \dot{\varepsilon} \) giving:

\[ \frac{\Delta P}{\rho g} = \left( \frac{E_v}{\rho g Q} \right)_{\text{entrance}} = 1.16 \frac{\delta^2 \dot{\varepsilon}^2}{8g} \]  

In straight sections of circular tubes, the head loss is given by (101):

\[ \left( \frac{E_v}{\rho g Q} \right)_{\text{straight section}} = f \frac{L' \cdot \nu^2}{D \cdot 2g} \]  

where \( f \) is the friction factor and \( L' \) is the length of the straight section. For laminar flows, \( f = 64/\text{Re} \). In terms of \( \dot{\varepsilon} \), and considering laminar flow, Eq. A.16 becomes:
Equation A.16 can be expressed in a more general way as:

\[
\frac{E_v}{\rho g Q} = K \frac{v^2}{2g}
\]  

(A-18)

where \( K \) is called the loss coefficient (101). For sudden expansions, \( K \) is given by:

\[
K = \left[ 1 - \left( \frac{D_1}{D_2} \right)^{2} \right]^{2}
\]  

(A-19)

where \( D_1/D_2 \) is the ratio of the diameters involved in the expansion (smaller and larger respectively). For all the jets considered, the value of \( K \) obtained from Eq. A-19 is close to 1. For our calculations, we will consider the worst case scenario \((K=1)\). From Eq. A-18 we obtain:

\[
\frac{E_v}{\rho g Q} = \frac{v^2}{2g}
\]  

(A-20)

The total pressure drop is calculated using Eq. A-9. Considering the different contributions given by the equations A.13, A.15, A.17 and A.20, we obtain:

\[
\frac{\Delta P}{\rho g} = \left( \frac{E_v}{\rho g Q} \right)_{\text{Total}} = \frac{3\eta_s \dot{e}}{\rho g} + \frac{1.16 \delta^2 \dot{e}^2}{8g} + \frac{16 \eta_s L \dot{e}}{\rho g D^2} + \frac{\delta^2 \dot{e}^2}{8g}
\]  

(A-21)

Finally, from Eq. A-21, the total pressure drop is calculated as:

\[
\Delta P = 3\eta_s \dot{e} + 1.16 \rho \frac{\delta^2 \dot{e}^2}{g} + 16 \eta_s \frac{L \delta}{D^2} \dot{e} + \rho \frac{\delta^2 \dot{e}^2}{g}
\]  

(A-22)
Under the conditions explored in this work, the most important contributions to the pressure drop are the losses due to entrance effects and to the sudden expansion. Figure A.3 shows the pressure drops measured in the opposed jets and the calculated values obtained using Eq. A-22. It is observed that the higher ΔP is obtained in jets 1 and 2, which are also the ones with smaller capillary diameter. In most cases, the values calculated with Eq. A-22 are an overestimate of the actual losses, whereas for jets 1, the experimental and the calculated values are practically the same. This means that regardless of the accuracy of our estimate, all the contributions considered for the calculation are important. Looking at Eq. A-22 one realizes for instance that the losses due to the straight section gain importance for smaller diameters (see third term of the right-hand side).
Figure A.3. Pressure drop as a function of strain rate for water in all the opposed jets. Closed circles are experimental $\Delta P$ values and open squares are calculated $\Delta P$ values.
Comparing jets 1 and jets 2, despite their similar dimensions, one noticeable difference between them is the expansion in jets 2 is more gradual. For illustration purposes, the losses for jets 2 are calculated after neglecting the last term of Eq. A-22. Figure A.4 shows the result of this assumption, and now the calculated and the experimental values are very close to each other. A good insight is obtained through these simple calculations as to what the causes of the pressure drop are for the different opposed jets, and also how the geometry strongly influences the results.

![Figure A.4](image.png)

Figure A.4. Pressure drop in jets 2 as a function of strain rate for water. Closed circles are experimental \( \Delta P \) values and open squares are calculated \( \Delta P \) values.

An important factor to consider is the sensitivity of the results to the value of \( D \). For example, Fig. A.5 shows the measured pressure drop for jets 1 as a function of the strain
rate calculated with Eq. A-7, using different values of $D$ whose difference is 0.05 mm, which is the accuracy of our measurements. It is observed that a slight difference in the value of $D$ represents a difference in $\dot{\varepsilon}$ such that there is a considerable difference in pressure drop for the same value of $\dot{\varepsilon}$.

Figure A.5. Pressure drop as a function of strain rate for water in jets 1. Values in the legend represent internal diameter of opposed jets ($D$).

Figure A.6 shows measured pressure drop curves for all the opposed jets as a function of the volumetric flow rate. This makes a good qualitative comparison, since the strain rate depends directly on the geometry of the system whereas the volumetric flow rate is measured directly. It is interesting to notice that when the diameter of the capillaries is above 0.75 mm, the pressure drop curves are very similar. However, once the diameter is
0.6 mm or lower, the rate at which the pressure drop increases with the volumetric flow rate is considerably higher. Thus, the lower the diameter, the higher the changes in \( \Delta P \) as we increase the flow rate.

![Diagram](image)

Figure A.6. Pressure drop as a function of volumetric flow rate in all the opposed jets.

A.3. Considerations for measuring the volumetric flow rate

As mentioned in the preceding chapters, the fluid flow rate is measured by recording the pressure drop of air flowing into the solution reservoir through a capillary tube connected to the reservoir and open to the atmosphere. This pressure drop (\( \Delta P_1 \)) is proportional to the flow rate of liquid (\( Q \)) leaving the reservoir and going into the test cell. This is true when the flow of air passing along the capillary is laminar (i.e. Hagen-Poiseuille flow). It was verified through a simple calculation that in the worst case
scenario (strain rates of the order of 6000 s\(^{-1}\)) a capillary of about 0.05 mm diameter is needed to have turbulent flow. This diameter is much smaller than what we normally use.

A capillary with internal diameter 0.44 mm was connected to the reservoir, and the following calibration curve is obtained:

\[ Q(\text{ml/s}) = 3.8367(V - V_{\text{off set}}) \]  

(A-23)

where \( V \) is the voltage indicated by the pressure transducer (the pressure transducer used spans the 0-1 psi range) and \( V_{\text{off set}} \) is the voltage that the apparatus indicate when it is not sensing any pressure difference (\( V_{\text{off set}} \) is normally about 2.27 V). Then, the strain rate is calculated using Eq. A-7. Figure A.7 shows curves of strain rate as a function of \( V \) for jets 1 and jets 3.

![Figure A.7. Strain rate as a function of voltage measured by the pressure transducer for two different opposed jets, using a capillary of 0.44 mm diameter.](image-url)
As seen by the slopes of the lines in Fig. A.7, the lower the diameter of the opposed jets, the more sensitive the calculated strain rate is to any voltage fluctuations of the transducer. Inspection of Eq. A-7 allows one to realize that a smaller diameter means a higher rate of increase of \( \dot{\varepsilon} \) with \( Q \). The consequence of this, is that the strain rates measured in this way using jets 1 are not accurate, since the error of the measurement is too high. Therefore, we need to decrease the rate at which \( \dot{\varepsilon} \) changes with \( V \) (equivalent to decrease the rate at which \( Q \) changes with \( V \)).

The Hagen-Poiseuille equation for air flowing through the capillary can be written as:

\[
Q = \frac{\pi D_0^4 \Delta P^*}{128\eta^* L_0}
\]  

(A-24)

where \( D_0 \) is the capillary diameter, \( L_0 \) is the length of the capillary, \( \eta^* \) is the viscosity of air and \( \Delta P^* \) is the pressure drop of air along \( L_0 \). Equation A.24 shows that the volumetric flow rate is directly proportional to the pressure drop. At the same time, the pressure drop varies linearly with the voltage measured by the transducer (as obtained during the calibration). If this is so, comparison of Eq. A-23 and Eq. A-24 indicates that decreasing the capillary diameter (\( D_0 \)) will definitely be the best option to reduce the rate at which \( Q \) changes with \( V \).

A capillary with \( D_0 < 0.44 \) mm was then used to replace the former one, and the calibration curve obtained is:

\[
Q(\text{ml/s}) = 1.3468(V - V_{\text{off-set}})
\]  

(A-25)
Figure A.8 shows curves of strain rate as a function of $V$ for jets 1 and jets 3, where for jets 1 the calibration is corresponds to the new capillary.

Figure A.8. Strain rate as a function of voltage measured by the pressure transducer for two different opposed jets, using two sizes of capillary.
APPENDIX B

EFFECT OF PEO MOLECULAR WEIGHT ON PRESSURE DROPS THROUGH OPPOSED-JETS

In this section, some additional results obtained with PEO are shown. These include: results with polymers of different average molecular weights and of polymers with same average molecular weight but different distribution of chain lengths.

B.1. Effect of Average Molecular Weight of PEO

Figure B.1 shows curves of pressure drop through the opposed jets as a function of strain rate for a fixed PEO concentration (1000 ppm) of two polymer samples with different $\overline{M}_w$:

![Graph showing pressure drop vs strain rate for different PEO concentrations.]

Figure B.1. Pressure drop in jets 5 as a function of strain rate for PEO solutions at $[\text{PEO}]=1000$ ppm. Values in the legend represent PEO average molecular weights ($\overline{M}_w$).
The results in Fig. B.1 show the dramatic difference in behavior of two polymer solutions whose $M_w$ are relatively close values. The value of $\dot{\varepsilon}_n$ for the higher molecular weight solution is considerably lower, indicating a very high degree of connectivity between the polymer chains. In this case fractions of longer polymer molecules are present in solution, which favor these interactions.

B.2. Effect of Chain Length Distribution

The polymer chain length distribution plays an important role in the results obtained in the opposed jets system. As seen in the previous section, longer chains in solution will have a dramatic effect on the behavior in extensional flow. In order to understand this behavior better, three different samples of PEO with the same $M_w$ are compared. In Table B.1 the samples are identified:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Polysciences</td>
</tr>
<tr>
<td>2</td>
<td>Polysciences</td>
</tr>
<tr>
<td>3</td>
<td>Scientific Polymer Products</td>
</tr>
</tbody>
</table>

Table B.1. Samples of PEO with same $M_w$ ($4 \times 10^6$)

Figure B.2 shows the results obtained through the opposed jets for these three samples. It is observed that for the same polymer concentration (same number of polymer chains in solution) the solution can behavior goes from dilute solution (sample 1) to a
solution where strong coil-coil interactions occur, inducing transient network formation from the lower values of strain rate (sample 2). This behavior denotes that there must be much longer chains present in the solution of sample 2 as compared to those for samples 1 and 3 for which there is none or weaker interactions respectively.

Notice that samples 1 and 2 were obtained from the same manufacturer (see table A.1) and also the same catalog number. However, they show dramatic differences when flowing through the opposed jets. This result proves that repeatability from batch to batch is not easy to obtain when producing PEO. Even though the same $M_w$ is obtained, the distribution of chain lengths is evidently very different. In addition, this result also indicates the high sensitivity of the opposed jets system to such differences between the samples.
Figure B.2. Pressure drop as a function of strain rate in jets 1 for PEO solutions of the samples shown in Table B.1 at [PEO]=300 ppm.
APPENDIX C

EFFECT OF SDS PURITY ON PRESSURE DROPS THROUGH OPPOSED-JETS

In this section, results in Jets 4 obtained with PEO/SDS solutions with and without NaCl are shown for two different SDS samples. The PEO is a polydisperse sample provided by polysciences with $\overline{M_w} = 8 \times 10^6$. The two SDS samples are described in table C.1:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Manufacturer</th>
<th>Purity (%)</th>
<th>Amount of SDS (%)</th>
<th>Other Surfactants in Sample*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sigma</td>
<td>99</td>
<td>99</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Sigma</td>
<td>95</td>
<td>62</td>
<td>28% of C_{14}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6% of C_{16}</td>
</tr>
</tbody>
</table>

* C_{14} and C_{16} are analog to SDS, but instead of 12 carbon atoms, the alkyl chains have 14 and 16 carbon atoms respectively

Table C.1. Characteristics of the SDS samples.

C.1. PEO/SDS solutions

Figure C.1 shows curves of pressure drop through the opposed jets as a function of strain rate for solutions with 100 ppm PEO and 6.2 mM SDS. Since this SDS concentration is higher than the CAC, interactions are already present, as verified when comparing the PEO/SDS solutions with the solution of pure polymer. However, it is evident that these interactions are quite different. The critical strain rate for transient
entanglement formation is very low for both solutions, but the increase in pressure drop is more abrupt for sample 2 at low strain rates. It is expected that the presence of surfactant molecules with longer alkyl chains would induce formation of larger aggregates that are able to promote interactions with other polymer chains more easily. A consequence of this would be that the resulting networks are stronger than those formed in the sample 1 solution. Besides, the CAC for sample 2 may be expected to be lower than for sample 1, so a larger number of aggregates might be present along the PEO chains in this case.

![Graph showing pressure drop in jets as a function of strain rate for PEO/SDS solutions at [PEO]=1000 ppm and [SDS]=6.2 mM.](image)

Figure C.1. Pressure drop in jets 4 as a function of strain rate for PEO/SDS solutions at [PEO]=1000 ppm and [SDS]=6.2 mM.
C.2. PEO/SDS in NaCl solutions

Figure C.2 shows curves of pressure drop through the opposed jets as a function of strain rate for 0.1 M NaCl solutions with 100 ppm PEO and 6.2 mM SDS. In this case, solutions of both samples show steep increases in pressure drop compared to the pure polymer solution. Due to the presence of salt, the aggregation starts at a lower surfactant concentration, the aggregation number is higher and the number of micellar aggregates per PEO molecule is larger than in the absence of salt due to electrostatic screening of the charges. All these factors are consistent with the promotion of strong intermolecular interactions, which are noticeable at very low strain rates. This is especially observed for sample 1 but not for sample 2, for which the presence of salt does not seem to affect to the same extent. However, looking at the shape of the curves for sample 2 in Figs. C.1 and C.2, where the $\dot{\varepsilon}_n$ value is so low and the increase in pressure drop is so abrupt at the lower strain rates, it is reasonable to assume that saturation of the sensitivity of the experimental setup to the presence of surfactant has already been reached. This is also observed in Fig. 2.10 where in the presence of salt, such saturation occurs when the SDS concentration is 6.0 mM. Therefore, the similarity between the curves in Fig. C.2 is likely to be due to such saturation in experimental setup sensitivity and not to suppression of the effect of the surfactant alkyl chain length in the presence of salt.
Figure C.2. Pressure drop in jets 4 as a function of strain rate for PEO/SDS solutions in 0.1 M NaCl at [PEO]=1000 ppm and [SDS]=6.2 mM.
APPENDIX D

USE OF STRUCTURAL MODELS TO REPRESENT THE RHEOLOGICAL BEHAVIOR OF POLYMER/SURFACTANT SOLUTIONS

Some additional results on the application of molecular models are shown in this section. Basically, the same models used in Chapter VI are used, but considering PEO samples with other molecular weights. The data of CAC and PSP used for the calculations in Chapter VI is presented as well. Table D.1 shows the values obtained for all the PEO samples used in the shear flow experiments.

<table>
<thead>
<tr>
<th>$M_w$ of PEO</th>
<th>[PEO] (ppm)</th>
<th>CAC (mM)</th>
<th>PSP (mM)</th>
<th>No NaCl in solution</th>
<th>0.1 M NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>600,000</td>
<td>3000</td>
<td>0.6</td>
<td>6.0</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4000</td>
<td>1.8</td>
<td>12.0</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>1,000,000</td>
<td>400</td>
<td>4.8</td>
<td>12.0</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>3.6</td>
<td>13.2</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>4.8</td>
<td>13.2</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>4.8</td>
<td>19.2</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>4.8</td>
<td>20.4</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>6.0</td>
<td>25.2</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>2,000,000</td>
<td>250</td>
<td>4.8</td>
<td>9.6</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>6.0</td>
<td>10.8</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>6.0</td>
<td>15.6</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>4,000,000</td>
<td>50</td>
<td>4.8</td>
<td>7.8</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>4.8</td>
<td>8.4</td>
<td>X</td>
<td></td>
</tr>
</tbody>
</table>

Table D.1. Values of CAC and PSP obtained from shear viscosity data for several PEO samples.
Table D.1. (continued). Values of CAC and PSP obtained from shear viscosity data for several PEO samples.

For calculations with the extensional flow data the CAC used was 4.5 mM.

Figures D.1 and D.2 show results of $\eta_l / \eta_{l,PSP}$ as a function of $([SDS]-CAC)/[PEO]$ for the PEO sample with $M_w=1\times10^6$ in the absence and in the presence of NaCl respectively. There is a good scaling of the data, similarly to what is observed in Fig. 6.25. Figure D.3 shows $\eta_l / \eta_{l,PSP}$ as a function of $([SDS]-CAC)/[PEO]$ for the PEO sample with $M_w=2\times10^6$, and Figs. D.4 and D.5 for the sample with $M_w=4\times10^6$ in the absence and in the presence of NaCl respectively. It is noticed that as $M_w$ increases, the data does not fit to a unique curve.
Figure D.1. Normalized interaction viscosity of PEO/SDS solutions as a function of the ratio of SDS complexed and PEO ($\bar{M}_W = 1 \times 10^6$). Values in the legend represent PEO concentrations.

Figure D.2. Normalized interaction viscosity of PEO/SDS solutions in 0.1 M NaCl as a function of the ratio of SDS complexed and PEO ($\bar{M}_W = 1 \times 10^6$). Values in the legend represent PEO concentrations.
Figure D.3. Normalized interaction viscosity of PEO/SDS solutions as a function of the ratio of SDS complexed and PEO ($\overline{M}_w = 2 \times 10^6$). Values in the legend represent PEO concentrations.

Figure D.4. Normalized interaction viscosity of PEO/SDS solutions as a function of the ratio of SDS complexed and PEO ($\overline{M}_w = 4 \times 10^6$). Values in the legend represent PEO concentrations.
Figure D.5. Normalized interaction viscosity of PEO/SDS solutions in 0.1 M NaCl as a function of the ratio of SDS complexed and PEO (\(\bar{M}_w = 4 \times 10^6\)). Values in the legend represent PEO concentrations.

Figures D.6 to D.8 show results of \(\frac{R_g}{R_g,eq}\) as a function of \(N_r\). The radius of gyration of the polymer when surfactant aggregates are formed along the PEO chains tends to increase as the number of aggregates per polymer chain increases for all the different samples. However, the results indicate that in the presence of salt, a more contracted conformation of the polymer chains of the PEO with higher molecular weight may be induced by the presence of SDS.
Figure D.6. Relative change in polymer radius of gyration as a function of the number of surfactant molecules per polymer chain for PEO/SDS solutions in the absence and in the presence of 0.1 M NaCl (for PEO: $\overline{M}_w = 1 \times 10^6$). Data from shear flow experiments (2).

Figure D.7. Relative change in polymer radius of gyration as a function of the number of surfactant molecules per polymer chain for PEO/SDS solutions (for PEO: $\overline{M}_w = 2 \times 10^6$). Data from shear flow experiments (2).
Figure D.8. Relative change in polymer radius of gyration as a function of the number of surfactant molecules per polymer chain for PEO/SDS solutions in the absence and in the presence of 0.1 M NaCl (for PEO: $\bar{M}_w = 4 \times 10^6$). Data from shear flow experiments (2).
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