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Porous media flow of poly(ethylene oxide)/sodium dodecyl sulfate mixtures

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Summary

In this work, the porous media flow of solutions of mixtures of Poly(ethylene oxide), PEO, and Sodium Dodecyl Sulfate, SDS, was studied. Aqueous solutions of PEO exhibited the well known critical extension thickening effect when flowing through disordered packings of glass spheres. Upon addition of SDS to a solution of fixed PEO concentration, the extension thickening of the mixture exhibits a maximum as a function of SDS concentration that mimics the shear viscosity behavior of the polymer-surfactant mixture. However, when NaCl is added to the mixture, higher extension thickening effects at relatively low SDS concentrations were detected, in spite of the fact that the shear viscosity of the mixtures was about the same as that of equivalent PEO/SDS solutions in deionized water. The results were rationalized in terms of how the formation of SDS micellar aggregates along the PEO chain can alter the ability of the polymer to form transient entanglement networks, which is the cause of the extension thickening behavior.

Keywords: Porous media flow, Poly(ethylene oxide), Sodium Dodecyl Sulfate, Polymer/Surfactant Mixtures, Transient networks.

Introduction

The flow of polymer solutions through porous media is relevant to a wide variety of practical applications. A particularly interesting one is enhanced oil recovery, where both high molecular weight polymers and surfactants are employed (1).

One of the most relevant aspects of the flow of polymer solutions through porous media is the increase in flow resistance obtained beyond a critical flow rate for solutions of flexible polymers. This increase has been attributed to the extensional nature of the flow field in the pores caused by the successive expansions and contractions that a fluid element experiences as it traverses the pore space, and by the presence of multiple stagnation points (2).

The relation between pressure drop and superficial velocity in flow through porous media made up of sphere packings is commonly represented in dimensionless form in terms of the resistance coefficient, which is a dimensionless ratio between pressure drop and superficial velocity, defined by

$$\Lambda = \frac{d^2 \phi^3 (\Delta P / L)}{\mu v (1 - \phi)^2} \tag{1}$$

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In this equation, ΔP is the pressure drop over a length L of porous medium, ϕ is the porosity (i.e., ratio of pore volume/total volume of the medium), d is the particle diameter, μ is the viscosity of the fluid, and v is the superficial velocity. If the Reynolds number is defined as

$$\mathrm{Re} = \frac{\rho v d}{\mu(1-\phi)} \tag{2}$$

where ρ is the density of the fluid, then Newtonian fluids satisfy the following relation

$$\Lambda = A + B\,\mathrm{Re} \tag{3}$$

A result consistent with Eq. 3 and previous literature (3) is shown in Figure 1 for water flowing through a disordered packing of glass spheres of 1.1 mm diameter.

The extension thickening behavior displayed by aqueous solutions of a high molecular weight poly(ethylene oxide), PEO ($M_v=3\mathrm{x}10^6$ g/gmol), when flowing through a disordered packing of 1.1 mm glass spheres is shown in Figure 1. The solutions display a pseudo-Newtonian behavior at low Reynolds number, with nearly constant values of Λ. The fact that Λ was calculated using the viscosity of the solvent in Eq. 1 accounts for the difference in Λ values at very low Reynolds number (which we shall term Λ_0) between the water curve and the PEO solution curves for concentrations equal to or higher than 250 ppm. In other words, the shear viscosity of those solutions is higher than that of water. If a concentration of PEO lower than 100 ppm is used, then the Λ_0 values are identical to those of water.

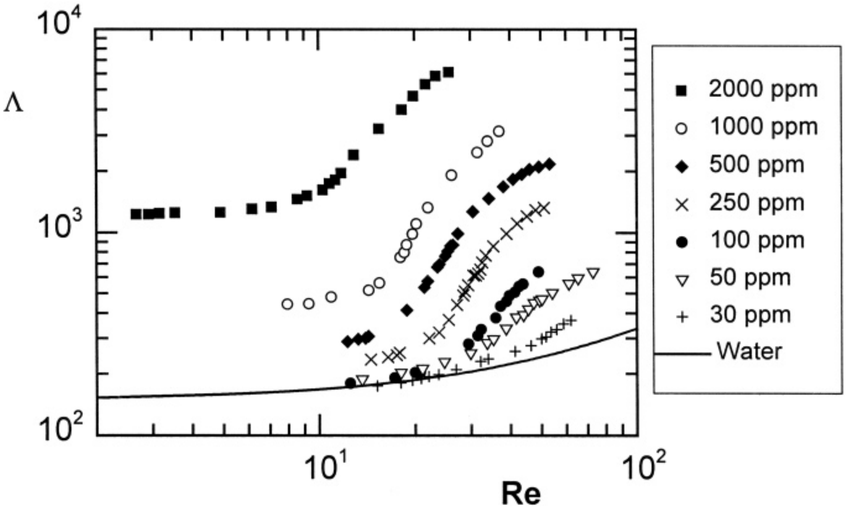

Figure 1. Resistance coefficients for water and aqueous solutions of PEO.

The rapid increase of Λ with Re beyond a specific value of the Reynolds number (usually referred to as Reynolds "onset", Reo), as shown in Figure 1, has been recently interpreted as arising from the formation of transient entanglement networks of polymer molecules induced by the elongational flow in the pores (this and other possible causes of extension thickening are addressed in detail in references 2 and 4). This extension thickening behavior has been extensively studied in the past for PEO and other high molecular weight flexible polymers in porous media flows (2, 4-5).

It is well known that solutions of mixtures of certain polymers and surfactants can exhibit unusual molecular interaction effects, whose nature has been the subject of investigation for several decades (6). In particular, the interactions between PEO and anionic surfactants (typically Sodium Dodecyl Sulfate, SDS) have been extensively explored (6-9). However, the flow behavior of such systems through porous media or other elongational flow situations has not yet been reported, as far as the authors are aware. It is the objective of the present communication to report experimental results on the flow of mixtures of PEO and SDS through disordered packings of glass spheres.

Experimental

The porous medium employed in the experiments consisted of disordered packings of monodisperse glass spheres of 1.10 mm in diameter. The experimentally determined porosity was 0.37. Pressure drops were recorded between the entrance and exit sections of the medium, formed by a Plexiglas cylinder of 20 mm internal diameter and 31 cm length. The experiments were conducted at 22 °C. More details about the experimental set up and measuring techniques have been given elsewhere (4). The PEO employed was supplied by Polysciences ($M_v=3x10^6$ g/gmol). All polymer solutions were prepared by carefully dissolving in deionized and distilled water (or the corresponding NaCl solution) the required quantity of polymer and SDS in powder form with minimum agitation (in order to avoid mechanical degradation of the polymer) during 24 hours. This time was needed to ensure complete dissolution of the polymer and maximum SDS/PEO interaction. All the solutions prepared were optically transparent and no apparent signs of gel formation or phase segregation were detected. Therefore, we consider that all the PEO/SDS aqueous solutions were a single phase after preparation. The Critical Aggregation Concentration (CAC, the concentration at which the surfactant starts to bind to the polymer) for the system PEO/SDS has been reported to be 5.7 mM (6), and in a recent conductimetric study values in the range 4.8 to 5.6 mM were found (9).

Results and Discussion

Porous media flow behavior of PEO and SDS solutions

Figure 2 shows the effect of varying the amount of SDS added to a PEO solution of 250 ppm. The 250 ppm PEO solution without SDS exhibits the typical extension thickening behavior of a high molecular weight flexible polymer, as shown in Figure 1. Upon addition of SDS, the resistance coefficient curves do not change appreciably if the SDS concentration is small (2.1 and 4.1 mM SDS). However, the addition of SDS at concentrations greater than or equal to 6.2 mM produces changes in flow behavior that cause the extension thickening to appear at lower Reynolds numbers than for the pure PEO solution. In addition, the resistance coefficients increase substantially as the SDS concentration is increased. It should be mentioned that the SDS concentrations used in this work are of the same order of magnitude of the critical micelle concentration of SDS in water (8.2 mM), so that the results in Figure 2 correspond to SDS concentrations that are much lower than those required to cause changes in the solution shear viscosity in the absence of polymer, which occurs at concentrations sufficiently high to induce the formation of cylindrical micelles (8).

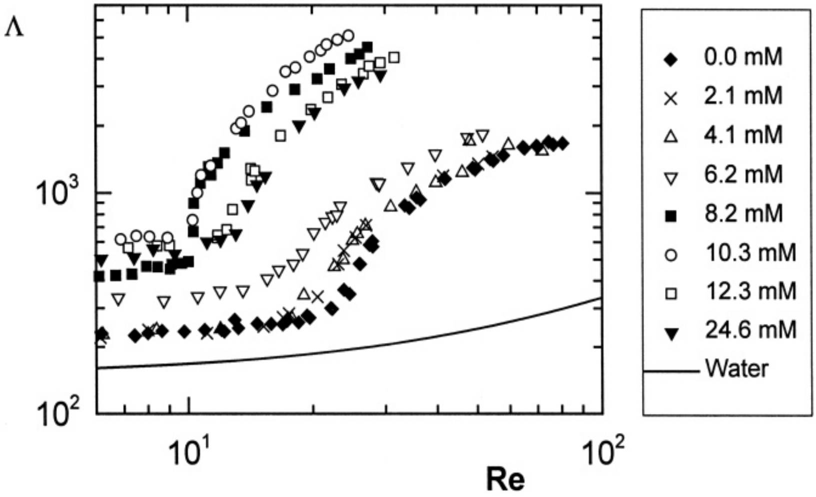

Figure 2. Resistance coefficients for PEO/SDS aqueous solutions at the indicated concentrations of SDS (250 ppm PEO).

The change induced by SDS in the porous media flow of PEO beyond a certain concentration is quite complex. The change of the Λ_0 values, which should be proportional to the solution shear viscosity (2), indicate that the apparent shear viscosity of the solution increases up to a maximum at an SDS concentration of 10.3 mM. Further addition of SDS up to 24.6 mM causes a slight decrease in Λ_0. This behavior can be rationalized when compared to literature reports on shear viscosity measurements for similar PEO/SDS solutions. For instance, Chari et al. (8) have measured the variation of shear viscosity with SDS concentration for PEO/SDS aqueous solutions. They have found that the shear viscosity goes through a maximum upon increasing SDS concentration at a constant PEO concentration. This maximum value has been reported to be independent of the PEO molecular weight but has been found to be linearly dependent on the PEO concentration (8).

If the shear viscosity of the solution were used instead of the solvent viscosity in Eq. 1, then all the PEO curves of Figure 2 should start from the water curves at low Reynolds numbers (5). Based on this, we have calculated an apparent shear viscosity of the solution (η_0^*) as the value of μ that would make the low Reynolds number asymptotes of the PEO resistance coefficients all equal to the water value. This apparent shear viscosity is plotted in Figure 3 as a function of SDS concentration. In the same figure, the SDS concentration at which a maximum shear viscosity is obtained for a 250 ppm PEO concentration is also indicated (dotted line). This value was calculated to be 11.8 mM by interpolating data presented by Chari et al. (8) for PEO/SDS solutions with polymers of different molecular weights. It can be seen that the observed maximum for η_0^* occurs around the same SDS concentration.

The mechanism behind the viscosification of PEO solutions upon addition of SDS has been attributed to the formation of a SDS/PEO molecular complex, a hypothesis that is still somewhat controversial (9). A model based on references 8 and 9 that explains the behavior of the SDS/PEO mixtures is presented in Figure 4. The model illustrates a sequence of events upon increasing SDS concentration, which are explained below.

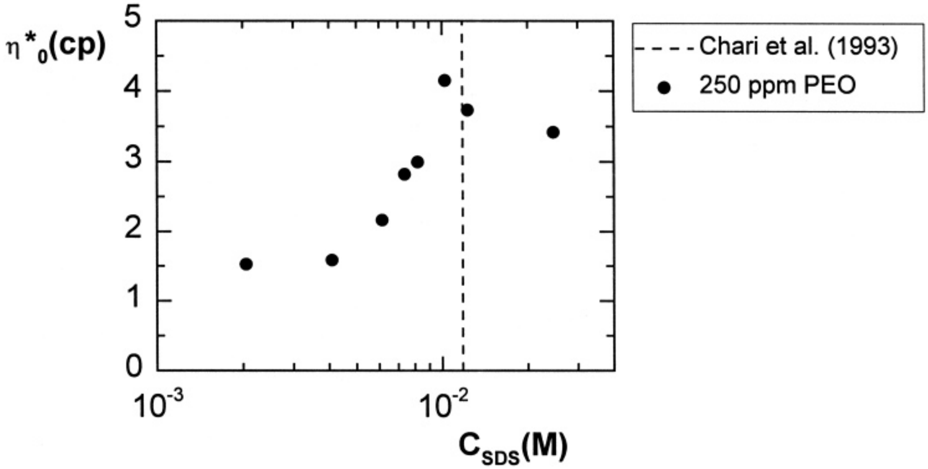

Figure 3. Apparent shear viscosity (derived from Λ_0 values of Fig. 2) as a function of SDS concentration. The vertical line represents the concentration of SDS for maximum shear viscosity (PSP) calculated from the shear viscosity data reported by Chari et al. (8).

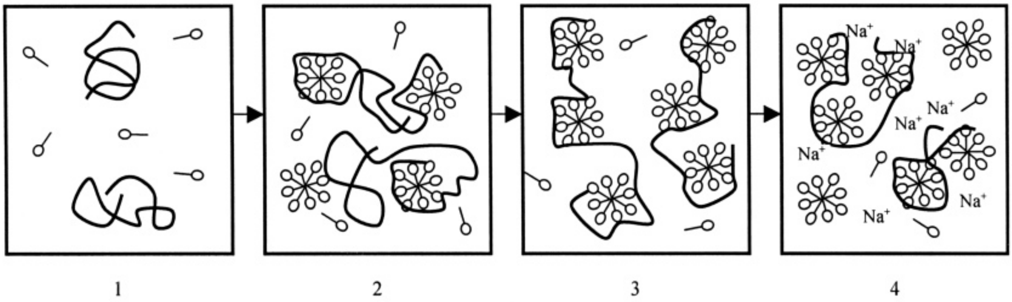

Figure 4. A schematic model showing the formation of a PEO/SDS complex, SDS concentration increases from left to right; 1: C_{SDS}<CAC; 2: C_{SDS}≥CAC; 3: C_{SDS}=PSP; 4: C_{SDS}≥PSP (see text).

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 "pseudopolycation" in which positive charges are distributed along the polymer coil (see ref. 7). 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 (i.e., the CAC), the SDS and PEO molecules are dissolved without intermolecular interactions (Figure 4.1). As the concentration of SDS in the solution increases, the concentration of sodium cations in solution also increases and the pseudopolycation is formed. At a specific SDS concentration (the CAC), surfactant aggregates are formed along the polymer chains. The hydrophilic, negatively charged ends of the micellar aggregates associate with the positive charges along the PEO chain (Figure 4.2). Since the micellar aggregates are negatively charged, they repel each other and the polymer coils expand. The expansion of the polymer coils in solution produces an increase in solution viscosity. As the SDS concentration increases, the number of attached micellar aggregates also increases and the polymer coils keep expanding, which consequently causes an increase in solution viscosity. Eventually, a saturation point is reached (Figure 4.3). At this point, the macromolecules have the maximum possible number of micellar aggregates attached. This is known as the Polymer Saturation Point (PSP), and the viscosity of the solution reaches an absolute maximum. 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 contraction of the coils, which in turn leads to a moderate decrease in solution viscosity (Figure 4.4).

The results in Figure 3 are consistent with the model presented. Not only the maximum in apparent shear viscosity occurs at the PSP, but also noticeable increases in apparent shear viscosity occur only at SDS concentrations higher than 4-6 mM (i.e., at concentrations higher than the CAC of the system, see experimental).

The results in Figure 2 also yield valuable information on the effects of adding SDS to the PEO on the extension thickening behavior. Qualitatively, the extension thickening effect follows a trend dictated by the apparent shear viscosity of the solution. The largest degree of extension thickening at the lowest Reo value is found at 10.3 mM SDS. The Reo decreases in Figure 2 as the SDS concentration increases, going through a minimum value at 10.3 mM, which is the PSP. A decrease in Reo is directly related to an increase in the disentanglement time of the chains involved in the formation of transient networks (2, 10). In this case, the increase is due to the expansion of the coils as the SDS concentration increases. Such expansion increases the coil-coil overlap of the system. When the SDS concentration increases beyond the PSP, the coils start to contract and the Reo in Figure 2 starts to increase just as the shear viscosity decreases.

Effect of NaCl addition to the PEO/SDS solutions

It is well known that the CAC is lowered, the size of the surfactant micelles increases and the number of micellar aggregates attached to a polymer chain also increases with the ionic strength of the solution (6, 9). For this reason, we decided to examine the behavior of the PEO/SDS solutions in the presence of 0.1 M NaCl. The concentration of PEO was kept constant at 250 ppm and the SDS concentration was varied in a wide range. The results are presented in Figure 5. The PEO solution in the absence of surfactant exhibits the same resistance coefficient with and without NaCl (2). At a very low SDS concentration (2.1 mM), the extension thickening was shifted to a higher Reo value and the Λ_0 to a slightly lower value than those of the pure PEO solution. In other words, the solution behaves as if the PEO coils had contracted. Since the presence of NaCl does not affect the PEO coil dimensions, one possible explanation could be that if the CAC is lower than 2.1 mM (values of 1.4 mM have been reported for different PEO/SDS/NaCl solutions with 0.045 M NaCl in ref. 9), intramolecular links caused by the presence of very few SDS micellar aggregates per coil could lead to a coil size reduction.

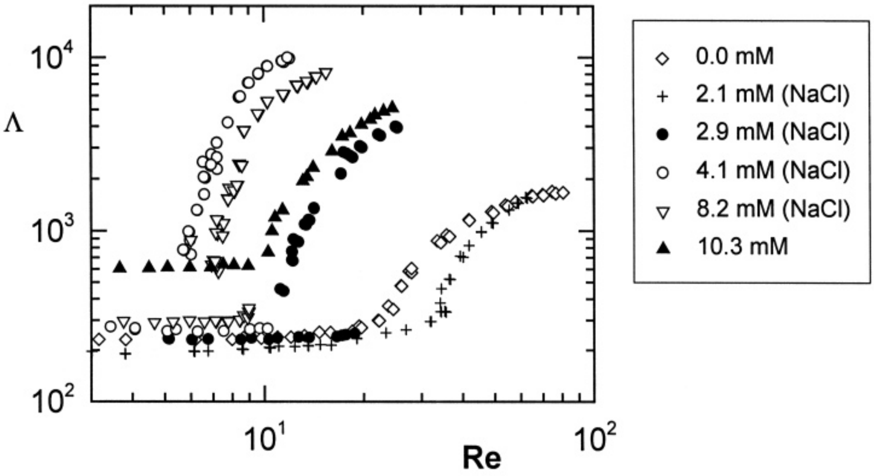

Figure 5. Resistance coefficients for aqueous PEO/SDS/NaCl solutions at the indicated concentrations of SDS (250 ppm of PEO and 0.1 M NaCl where indicated)

Upon increasing the SDS concentration to just 2.9 mM, the extension thickening is now produced at a Reo lower than for the pure PEO solution. This PEO/SDS/NaCl solution exhibits nearly the same shear viscosity as pure PEO solution, since the Λ_0 values of both solutions are identical. However, at a Reynolds number of about 19, further increases in the pressure drop (and hence Λ) produce a reduction in flow rate. This behavior is a result of a flow instability brought about by a possible "plugging" of some of the pores due to the formation of a "transient gel" or strong entanglement network. After this plugging effect occurs at a specific Reynolds number, the flow rate drops and a large extra pressure is required to make the solution flow at the same Reynolds number. The same effect is seen at higher SDS concentrations. It should be pointed out that, in the unstable flow region, data points presented in Figure 5 are an average of many readings.

Chari et al. (8) reported the measurements of shear viscosity of PEO/SDS/NaCl solutions with different salt contents. The viscosity at the PSP concentration was reduced from about 4 mPa s to about 1 mPa s when the concentration of NaCl was increased from 0 to 0.1 M. Such behavior was explained by coil contraction. In our case, the apparent shear viscosity of the solutions with NaCl is also much smaller than the equivalent solutions without salt (compare the Λ_0 values of all the curves in Figures 2 and 5). However, the extension thickening effect is stronger and more critical in the presence of the electrolyte.

The solution with 10.3 mM SDS but without salt was included in Figure 5 for comparison purposes. Notice how the 4.1 and 8.2 mM curves with NaCl have a Reo that is similar to that of the 10.3 mM solution without salt. However, the apparent shear viscosity of the solutions in salt resembles that of the pure PEO solutions, and their degree of extension thickening is much stronger than the 10.3 mM solution without salt. This is a puzzling result, since one would expect a lower probability of coil-coil overlap if the polymer coils have contracted (as explained above). There must be a new factor coming into play that is allowing the system to behave as a connected three dimensional network beyond a specific strain rate. It is very tempting to speculate that the increased number of micellar aggregates per polymer chain (upon NaCl addition) as well as their greater aggregation number (which produces a bigger micellar size) may be causing the association of polymer molecules through attachment of the same micellar aggregate to different polymer chains. Such situation may only happen during flow when the alignment of the polymer coils reaches a certain degree. Such intermolecular associations between polymers and surfactants have been proposed to explain shear thickening and gel formation in other polymer/surfactant systems (6). In more pragmatic terms, our results suggest a way to greatly increase the extension thickening of PEO solutions in pore flow with a small addition of SDS in ionic media, with a minor increase in shear viscosity.

Conclusions

The results obtained in this work demonstrate that the extension thickening behavior of a polymer solution in an elongational flow situation can be manipulated by adding an ionic surfactant that forms micellar aggregates along the polymer chains. The ionic environment of the solution has a dramatic effect on the extension thickening behavior of these systems.

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