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Shear and extensional rheology of solutions of mixtures of poly(ethylene oxide) and anionic surfactants in ionic environments

Miguel F. Torres [a], Alejandro J. Müller [a,*], Miklos A. Szidarovszky [b], A. Eduardo Sáez [b,*]

[a] *Grupo de Polímeros USB, Departamento de Ciencias de los Materiales, Universidad Simón Bolívar, Caracas 1080A, Venezuela*
[b] *Department of Chemical and Environmental Engineering, University of Arizona, Tucson, AZ 85721, USA*

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ABSTRACT

Interactions between a high molecular weight poly(ethylene oxide) (PEO) and the anionic surfactant sodium dodecyl benzene sulfonate (SDBS) in aqueous solutions were investigated by shear and extensional rheometry. Results for mixtures between PEO and sodium dodecyl sulfate (SDS) are also presented for comparison purposes. Addition of anionic surfactants to PEO solutions above the critical aggregation concentration (CAC), at which micellar aggregates attach to the polymer chain, results in an increase in shear viscosity due to PEO coil expansion, and a strengthening of interchain interactions. In extensional flows, these interactions result in a decrease of the critical shear rate for the onset of the characteristic extension thickening of the PEO solutions that is due to transient entanglements of polymer molecules. The relaxation times associated with these transient entanglements are not directly proportional to the shear viscosity of the solutions, but rather vary more rapidly with surfactant concentration. In the presence of an electrolyte, coil contraction results in lower shear viscosities and a decrease in the extension thickening effects at surfactant concentrations just beyond the CAC. The relaxation times associated with transient entanglement reach a minimum at the same surfactant concentration as the shear viscosity, which indicates that coil contraction is responsible for the observed effects in both types of flow. However, the increase in extensional-flow entanglement relaxation times is much more abrupt than the decrease in shear viscosity. All these results point to a greater sensitivity of extensional flows on the molecular conformation of PEO/surfactant complexes.

1. Introduction

Extensive research has shown that polymer/surfactant interactions can have a significant effect on polymer solution rheology. Mixtures between high-molecular weight poly(ethylene oxide) (PEO) and the anionic surfactant sodium dodecyl sulfate (SDS) have been used as model systems in the study of rheological behavior of polymer/surfactant interactions. It has been widely reported that the formation of micellar aggregates along the PEO chain causes coil expansion due to electrostatic repulsion between micelles, which leads to an increase of the shear viscosity of the PEO solutions [1–5, and references therein]. The micellar aggregates attached to the polymer chain form at a critical aggregation concentration (CAC) that is substantially lower than the critical micelle concentration (CMC) of the surfactant, which is typical of many polymer/surfactant mixtures, especially those between anionic surfactants and nonionic polymers. The increase in size of the polymer coil due to the attached micelles, and the possible interchain temporal cross links induced by the micellar aggregates also play a role in the viscosity increase with surfactant concentration beyond the CAC. Eventually, the viscosity reaches a maximum with surfactant concentration and it typically decreases at even higher surfactant concentrations. The decrease in viscosity has been associated with the screening of charges of the micellar aggregates by the relatively high concentration of counterions. The point of maximum viscosity has been identified with the saturation of polymer chains with micellar aggregates (polymer saturation point, PSP) [6,7], although this is not always the case: for high molecular weight samples of PEO (more than 1×10^6 g/mol), the maximum seems to precede the saturation point [8].

The presence of an additional electrolyte affects the nature and strength of PEO/SDS interactions. It is well known that the CMC and CAC of SDS decrease substantially in ionic solutions, while the micelle aggregation number increases [9]. High ionic strengths provide an environment that favors aggregation of hydrophobic groups. In addition, the presence of an excess of counterions (e.g., Na^+ when NaCl is the electrolyte) allows the micelles to grow due to electrostatic screening of their charges. Both the CMC and CAC

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* Corresponding authors.
E-mail addresses: amuller@usb.ve (A.J. Müller), esaez@email.arizona.edu (A.E. Sáez).

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uniformly decrease with NaCl concentration in the range 10^{-3} to 10^{-1} M. In fact, both concentrations vary following a scaling close to $[\mathrm{NaCl}]^{0.5}$ [10]. The association of counterions with the PEO/SDS complex becomes so strong for high molecular weight PEOs that the electrical conductivity of the solution can remain constant with addition of surfactant beyond the CAC [8].

Typically, an increase of the SDS concentration beyond the CAC in the presence of an electrolyte leads to a decrease in solution viscosity [11], which has been attributed to a contraction of the PEO coil when a few micelles are attached to it [5,12–14]. The fact that PEO coil contraction is strong enough to produce a viscosity reduction only in the presence of an electrolyte (the viscosity decrease has not been observed in PEO/SDS systems without salt) has been explained by the counterion's electrostatic screening of the micelles, which eliminates the opposite effect of coil expansion due to micelle repulsion [5]. Coil contraction due to electrostatic screening has been measured directly for various nonionic polymer/surfactant complexes in electrolyte solutions using light scattering techniques [15, and references therein].

At SDS concentrations significantly above the CAC, the viscosity starts increasing again due to the increase of the number of micelles attached to the PEO chain, which lead eventually to coil expansion. However, the shear viscosity levels achieved in the presence of an electrolyte are lower than for the pure PEO/SDS system, due once again to a decrease in micellar interaction by electrostatic screening [8].

The behavior of POE/SDS solutions in extensional flows reproduce some of the trends observed in shear flows. However, PEO solutions exhibit extension thickening above a critical strain rate, so that published observations pertain to the onset of extension thickening and the increase in the apparent elongational viscosity after extension thickening sets in. In a previous work [16], we reported a sizeable increase in the elongational viscosity of PEO/SDS solutions for SDS concentrations higher than the CAC. At the same time, addition of SDS decreases the critical strain rate for extension thickening, which is consistent with coil expansion. In the presence of NaCl, the critical strain rate decreased with SDS concentrations well above the CAC, but, contrary to the shear flow results reported above, the elongational viscosity increase in the extension thickening regime was more pronounced than without salt.

Mixtures of nonionic polymers with sodium dodecyl benzene sulfonate (SDBS) have not been studied as extensively as those with SDS. Hou et al. [17] used surface tension measurements to conclude that interactions between SDBS and PEO were similar to those observed in the PEO/SDS system. However, they report a binding ratio at the polymer saturation point of 0.038 moles of SDBS per mole of ethylene oxide unit, which is significantly lower than the 0.2 to 0.3 moles SDS per mole of ethylene oxide unit reported for the PEO/SDS system [18,19]. In addition, counterion binding has been reported to be much weaker on SDBS micelles [20]. Interactions between SDBS and polyvinyl pyrrolidone [21,22] exhibit similar behavior as the PEO/SDS system. Nevertheless, in a previous work we found significant differences in behavior between the PEO/SDBS and PEO/SDS systems for very high molecular weight PEO (8×10^6 g/mol) in extensional flows: addition of SDBS to PEO solutions at concentrations below the CAC induced a strong increase of the critical strain rate for extension thickening, which might be a result of coil contraction [23]. This effect was observed both in the absence and presence of salt and with other sulfonated surfactant (an α-olefin sulfonate). Polymers of lower molecular weight (4×10^6 g/mol PEO and below) did not exhibit such behavior.

Even though shear rheology of PEO/anionic surfactant systems has been widely studied, and our group has reported data on extensional flows of PEO/SDS [16] and PEO/SDBS [23] solutions, we are not aware of a direct comparison of the rheological behavior of such mixtures in shear and extensional flows. The main objective of this work is to perform a comparison between the shear and extensional flow behavior of PEO/anionic surfactant systems with and without addition of an electrolyte (NaCl).

2. Experimental

Poly(ethylene oxide) with a nominal molecular weight of 4×10^6 g/mol was acquired from Polysciences. Sodium dodecyl sulfate (99% purity), sodium dodecyl benzene sulfonate (80%) and sodium chloride (99%) were obtained from Sigma-Aldrich. High purity sodium dodecyl benzene sulfonate (95%) was purchased from TCI. The SDBS used in the results is the 80% purity sample, unless specified otherwise.

The weight-averaged molecular weight of the PEO sample was determined by static light scattering using a multi-angle light scattering device (Wyatt Technologies Corp.) equipped with a 30 mW Ga/As laser at a wavelength of 690 nm. The change of refractive index of the solutions with PEO concentration was estimated from data presented by Polik and Burchard [6] to be $dn/dc = 0.134$ mL/mg. Dilute PEO solutions were prepared by dispersing the solid PEO into distilled deionized water and gently stirring for 24 h. The solutions were filtered through 0.45-μm Millipore membranes. The molecular weight measured was $\bar{M}_{\mathrm{w}} = 3.6 \pm 0.2 \times 10^6$ g/mol, and the average radius of gyration was $R_{\mathrm{g}} = 182 \pm 2.9$ nm at 25 °C.

Steady-state fluorescence measurements were performed in a Perkin-Elmer fluorescence spectrophotometer (LS-550B). The fluorescence probe used was pyrene (Sigma-Aldrich, 99%) at a concentration of 2.5×10^{-7} M. An excitation wavelength of 334 nm was used, and emission spectra were measured in the range 365–390 nm. The fluorescence intensity ratio between the first (373 nm) and third (383 nm) peaks of the spectrum (I_1/I_3) is sensitive to the micropolarity of the environment surrounding the pyrene in solution and, given the strong partitioning of pyrene into the hydrophobic cores of micelles, this ratio has been extensively used as an indicator of micelle formation [24]. Plots of I_1/I_3 vs surfactant concentration ([S]) show a transition around the critical micelle concentration. According to Aguiar et al. [25], this transition can be correlated using a Boltzmann sigmoid curve,

$$\frac{I_1}{I_3} = y_\infty + \frac{y_0 - y_\infty}{1 + e^{([\mathrm{S}]-[\mathrm{S}]_\mathrm{c})/A}} \tag{1}$$

where y_0 and y_∞ are the I_1/I_3 values at the low and high concentration plateaus, respectively, and A and $[\mathrm{S}]_\mathrm{c}$ are fitting parameters. It is generally acknowledged that $[\mathrm{S}]_\mathrm{c}$ (i.e., the concentration at the inflection point) represents the CMC (or the critical aggregation concentration, CAC, in the case of surfactant/polymer mixtures), although there are indications that this value might differ somewhat from the CMC or CAC determined by other techniques [25]. In this work, we take $[\mathrm{S}]_\mathrm{c}$ to be the CMC or CAC as a basis for comparison.

Simple shear flow experiments were conducted using a Rheometrics ARES shear rheometer with a double-wall Couette fixture. Solutions of PEO exhibited Newtonian behavior at concentrations below 500 ppm in the whole range of shear rates used (0–200 s^{-1}), and were shear thinning with a low-shear rate Newtonian plateau at higher concentrations (results not shown). Measurements reported here will be based on the low-shear rate Newtonian plateau in all cases. The standard method of Huggins and Kramer was used to determine the intrinsic viscosity of PEO solutions (e.g., see Macosko [26]). The intrinsic viscosity ($[\eta]$) was used to determine the viscosity-averaged molecular weight ($\bar{M}_{\mathrm{v}}$) using the Mark–Howink–Sakurada equation [27],

$$[\eta] = K\bar{M}_{\mathrm{v}}^{a} \tag{2}$$