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Shear and extensional rheology of solutions of modified hydroxyethyl celluloses and sodium dodecyl sulfate

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Abstract

This work reports on the rheology of aqueous solutions of hydroxyethyl cellulose (HEC) and three derivatives, in the presence of sodium dodecyl sulfate (SDS). The polymers employed were: a hydrophobically modified hydroxyethyl cellulose (HMHEC) containing hexadecyl grafts, a cationically modified hydroxyethyl cellulose (cat-HEC), containing glycidyl-trimethyl-ammonium grafts, and a polymer with both modifications (cat-HMHEC). Rheological measurements were performed in simple shear flow, oscillatory shear flow, opposed-jets flow and flow through porous media. The addition of surfactant increases intermolecular interactions between HMHEC molecules due to the formation of mixed micelles that bridge hydrophobic side groups from different polymer chains. These interactions lead to phase separation in an intermediate SDS concentration range and, at higher surfactant concentrations when a homogeneous phase was obtained, to higher shear and apparent extensional viscosities. Further surfactant addition eventually inhibits hydrophobe interactions due to electrostatic repulsion between micelles, leading to shear viscosities that are even lower than that of the original polymer solution. Hydrophobe interactions are inhibited by the relatively strong nature of flow in opposed-jets. The addition of cationic side groups confers the polymer a polyelectrolytic nature, which translates into higher shear and apparent extensional viscosities. Interchain interactions are strengthened by the presence of surfactant by the formation of intermolecular cross-links between polymer chains. © 2002 Published by Elsevier Science Ltd.

Keywords: Modified hydroxyethyl cellulose; Sodium dodecyl sulfate; Micellar aggregates

1. Introduction

The rheological properties of aqueous solutions of hydroxyethyl cellulose (HEC) and other water-soluble polymers can be controlled by modifying the polymer backbone with side chain attachments, such as ionic or hydrophobic groups. In general, modifications are tailored to cause an increase in viscosity that improves the use of the polymer as a thickener in food, cosmetic products, water-based paints and other industrial applications. Such a viscosity improvement is promoted by the interaction between the substituent groups on the polymer. In hydrophobically modified hydroxyethyl cellulose (HMHEC) [1–3], the thickening action is caused by the association of the hydrophobic side chains into an intermolecular transient network (Fig. 1). On the other hand, cationically modified HECs (cat-HEC) tend to behave like typical polyelectrolytes [4]: the viscosity enhancement is due to the repulsion of the charged groups along the chain, which expands the macromolecule.

Polymer–surfactant interactions have been systematically investigated as an additional aspect of rheology modification. Studies with HEC and sodium dodecyl sulfate (SDS) reveal that the surfactant forms micellar aggregates along the polymer chain at a critical aggregation concentration (CAC) of 6 mM at ambient conditions, which is appreciably lower than the critical micellar concentration (CMC) of SDS (8 mM at 20 °C) [2,5]. However, these associations do not have an appreciable effect on the shear viscosity of the solutions.

The effects of addition of anionic surfactants (such as SDS) to HMHEC vary substantially with surfactant concentration. At surfactant concentrations higher than the CAC, mixed micelles between the surfactant and the hydrophobic side chains form. Each mixed micelle contains more than one hydrophobic side chain, thus creating temporal cross-links between polymer molecules. This

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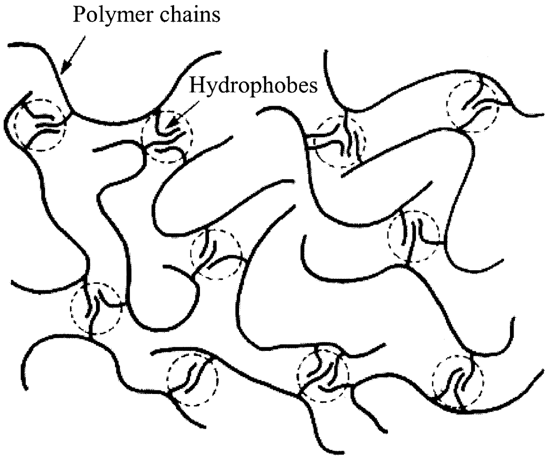

Fig. 1. Intermolecular network formed by interactions between hydrophobic groups in HMHEC.

association strengthens intermolecular interactions, leading to an increase in shear viscosity with surfactant concentration [2,6–8]. As the surfactant concentration is increased, the number of side chains per micelle decreases to the point that intermolecular associations of polymer molecules are inhibited, due to the electrostatic repulsion between attached micellar aggregates. As a consequence, the shear viscosity of the solution reaches a maximum and then decreases as surfactant concentration is further increased [8,9]. The inhibition of interchain interactions through hydrophobic side chains eventually might lead to a viscosity that is even lower than that of the pure polymer solution.

Polymer–surfactant interactions between cat-HEC and SDS have also been studied. The interaction mechanism is consistent with that observed in mixtures of polyelectrolytes and oppositely charged surfactants. The surfactant's hydrophilic end binds to the positively charged sites of the cat-HEC chain, and the hydrophobic ends of the bound surfactant molecules interact, forming cross-links between different polymer chains [10,11]. Intramolecular cross-links are also produced by this mechanism; this results in the contraction of the coil [3]. As is the case for HMHEC, the viscosity of solutions of cat-HEC and SDS increases with surfactant concentration beyond the CAC. A maximum is commonly not reached, since the solution tends to separate into two distinct phases: a gel-like phase with polymer–surfactant aggregates, and a low-viscosity phase [4]. If the SDS concentration is further increased, a one-phase system with decreasing viscosity is obtained [4,12].

Since cationic and hydrophobic modifications of HEC yield polymers with the same qualitative response to SDS addition in terms of viscosity increases beyond the CAC, it is attractive to consider the possibility of a polymer with both cationic and hydrophobic modifications (cat-HMHEC). In addition, more hydrophobic side chains could be grafted to cat-HEC than to HEC, due to the polyelectrolytic (more soluble) nature of the cat-HEC. Previous works have shown that an increase in the number of hydrophobic groups per chain of cat-HMHEC leads to sizeable increases in solution viscosity at a fixed SDS concentration [4].

The rheological characterization of solutions of polymer/surfactant mixtures is normally carried out using shear rheometry. However, extensional flows are important in applications for which these polymer solutions have potential uses, such as enhanced oil recovery [13] and coating flows. It is well known that chain conformation in solution plays a crucial role in determining the behavior of the polymer solution in an extensional flow field [14]. For example, solutions of flexible polymers are shear thinning, but the formation of transient entanglements make them extension thickening. Moreover, extensional flows represent an additional option to probe changes in polymer structure and intermolecular interactions brought about by chain modification and surfactant effects. One of the aims of this work is to study the extensional flow behavior of solutions of modified HECs and SDS.

The opposed-jets system has been used extensively in the study of extensional flow of polymer solutions [15–17]. 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 semi-flexible polymers, such as the HECs used in this work may undergo some deformation.

Tan et al. [18] used the opposed-jets system to study the behavior of hydrophobically modified alkali-soluble associative (HASE) polymers, which essentially consist of a polyacrylate backbone with hydrophobic side chains. The solutions were shear thinning, but extension thickening was observed for solutions of polymers with short-chain (C_{12}) hydrophobes.

Extensional flow can also be generated in a porous medium made up of disordered sphere packings. The successive expansions and contractions of the flow path, along with the multiple stagnation points, provide an extensional nature to this flow. However, extensive shear is also present due to the relatively large solid surface area.

In this work we study the rheological behavior of three kinds of modified HECs: hydrophobically modified HEC (HMHEC), cationically modified HEC (cat-HEC) and an HEC with both cationic and hydrophobic modifications in disordered distribution (cat-HMHEC). We consider simple shear flow conditions, oscillatory shear, and extensional flows (opposed-jets and porous media).

2. Experimental

2.1. Materials

Two different basic samples of HEC were used in this study: HEC1, with a molecular weight $\bar{M}_w = 300\,000$, generously provided by Hercules (Natrosol 250GR), and HEC2, with a molecular weight $\bar{M}_w = 560\,000$, generously provided by Clariant (Tylose H4000 G4 PHA). The molar substitution of ethylene oxide groups is 2.5 per anhydroglucose unit in HEC1 and 2.31 in HEC2. The HMHEC was also provided by Hercules (Natrosol Plus 330 CS) and the molecular weight should be similar to that of HEC1. The hydrophobic side groups are hexadecyl chains, present with a molar substitution of 0.01. The other two modified polymers, cat-HEC and cat-HMHEC, were especially prepared for us starting from HEC2 by Dr R. Krammer in the Research and Development Department of Clariant in Wiesbaden, Germany. They have the same molecular weight, $\bar{M}_w = 950\,000$. Both polymers have also the same molar substitution of cationic groups (0.34), which are glycidyl-trimethyl-ammonium chloride chains. In addition to the cationic groups, the cat-HMHEC has dodecyl chains in a random distribution with a molar substitution of 0.007.

SDS was the surfactant used, obtained from Baker. The salt used was analytical grade sodium chloride (99.99%) from Riedel–deHaën.

The aqueous polymer/surfactant solutions were prepared by dissolving first the surfactant and then adding the polymer. The resultant solution is stirred slowly but continuously for 24 h prior to use, to ensure complete polymer dissolution.

2.2. Equipment and procedures

For the simple shear experiments, a Rheometrics ARES shear rheometer with a double-wall Couette geometry was used to measure shear viscosity as a function of shear rate. Zero-shear-rate viscosity was determined from either the measured Newtonian plateau at low shear rates or by fitting the Ellis model to the data.

Low-amplitude oscillatory shear measurements were carried out in the same equipment. The frequency range used was 0.1–100 s^{-1}, at 0.5 strain.

The opposed-jets system consisted of two aligned glass capillaries with a separation $d = 1.21$ mm and an internal diameter $D = 0.6$ mm. The experimental setup is described in detail elsewhere [19]. The pressure drop of the liquid flowing through the jets is measured as a function of the apparent strain rate in the extensional flow field, calculated by

$$\dot{\varepsilon} = \frac{4Q}{\pi D^2 d} \tag{1}$$

where Q is the total volumetric flow rate going through the jets.

All the experiments consist of a controlled increase of strain rate starting from rest. Previous work [19] has shown that pressure drop vs. strain rate curves might exhibit hysteresis depending on how the flow is set.

Porous media flow experiments are conducted in the same equipment used previously with other polymers [14]. The porous medium employed is a Plexiglas cylinder, with 20 mm of internal diameter and 30 cm length, filled with a disordered packing of monodisperse glass spheres of 1.10 mm in diameter. The experimentally determined porosity was 0.37. The pressure drop between the entrance and exit sections of the medium was recorded as a function of superficial velocity. Results are reported in terms of the dimensionless resistance coefficient, Λ, defined by

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

In this equation, ΔP is the pressure drop over a length L of porous medium, ϕ is the medium porosity, d is the particle diameter, μ is the viscosity of the solvent (water), and v is the superficial velocity.

The rheological behavior of the solution is analyzed by measuring the resistance coefficient as a function of Reynolds number, defined as

$$Re = \frac{\rho v d}{\mu(1-\phi)} \tag{3}$$

where ρ is the density of the fluid.

All the experiments were carried out at 20 °C.

3. Results and discussion

3.1. Shear rheology: simple shear

In this section we report the experimental results obtained in shear flow measurements using the double-Couette geometry.

The hydrophobic side groups of the HMHEC increase the level of intermolecular interactions in shear flows over that of the original polymer (HEC1), as evidenced by the shear viscosity measurements shown in Fig. 2. Note that solutions of HEC1 behave approximately as Newtonian fluids in the

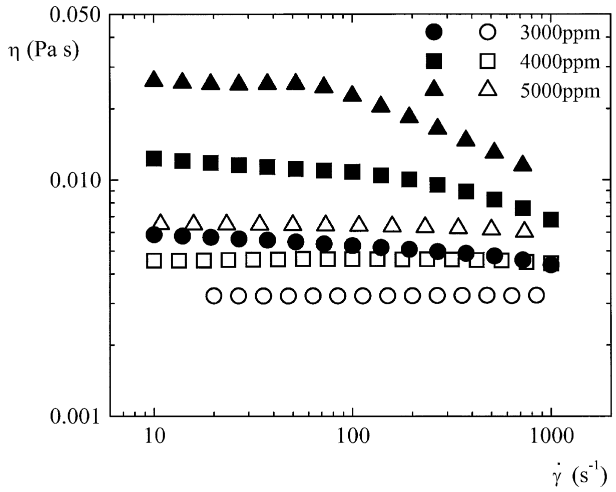

Fig. 2. Shear viscosity of solutions of HEC1 (open symbols) and HMHEC (filled symbols) at various polymer concentrations.

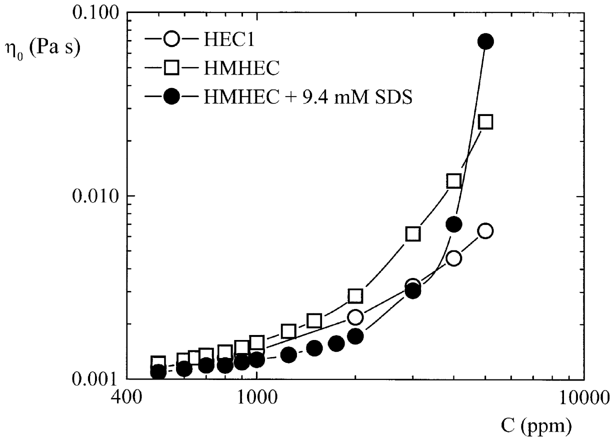

Fig. 3. Zero-shear-rate viscosity of solutions of HEC1, HMHEC and mixtures HMHEC + SDS as a function of polymer concentration.

range of strain rates explored, whereas solutions of HMHEC at the same concentrations are more viscous, and exhibit a degree of shear thinning that is enhanced at higher concentrations.

A comparison between the zero-shear-rate viscosities of HMHEC and HEC solutions is shown in Fig. 3. The zero-shear-rate viscosity of HMHEC is always above that of HEC1 in the range of concentrations explored. This indicates that possible intramolecular associations between hydrophobic side chains do not produce a decrease in viscosity.

The addition of SDS does not produce a measurable effect on the shear viscosity of HEC solutions, which also remains as a single-phase. Phase separation is observed upon addition of small concentrations of SDS to semi-dilute HMHEC solutions. A representation of the phase separation region is shown in Fig. 4, in which the zero-shear-viscosity of semi-dilute HMHEC solutions is presented as a function of SDS concentration. The solutions separate into a dilute phase and a gel-like phase. At the polymer concentrations employed (3000 and 5000 ppm) and in the absence of surfactant, the polymer molecules exhibit intermolecular interactions due to the presence of the hydrophobic side chain, as evidenced by their shear viscosity (Fig. 2). These interactions are micelle-like structures formed by the aggregation of hydrophobic side chains. Presumably, the amount and aggregation number of these structures are increased in the presence of SDS due to the formation of mixed micelles between SDS molecules and the hydrophobic side chains. This leads to the formation of highly cross-linked polymer domains that separate into the gel-like phase. As the SDS concentration is increased, the volume fraction of the gel-like phase increases until a homogeneous single-phase is obtained. These homogeneous solutions have a viscosity that is much higher than that of the HMHEC solution, but that decreases upon further addition of SDS (Fig. 4). The homogenization and viscosity decrease are a consequence of the decrease in the strength of intermolecular interactions between polymer chains due to a reduction in the number of hydrophobic side chains in the mixed micellar aggregates. Eventually, at high SDS concentrations, the viscosity of the solutions drops below the viscosity of the solutions of the pure HMHEC. At this point, micellar aggregates, consisting mainly of SDS molecules, shield hydrophobic side chains from interacting due to the electrostatic repulsion between aggregates.

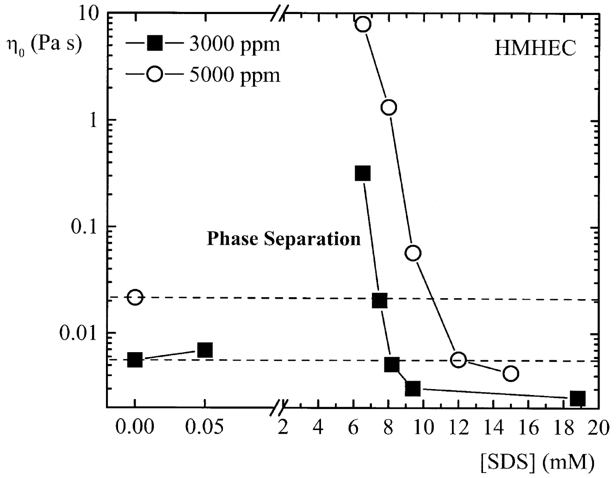

Fig. 4. Effect of SDS on the zero-shear viscosity of two HMHEC solutions. Measurements were not made in the two-phase region observed at low SDS concentrations. The horizontal dashed lines represent the zero-shear viscosity of the solutions without SDS.

It is interesting to point out that it takes only two hydrophobic side chains in a mixed micelle to strengthen considerably interchain associations, as demonstrated recently for mixtures between a HMHEC and cationic surfactants [8]. Upon surfactant addition, the viscosity reached a maximum when the average number of hydrophobes per mixed micelle was close to 2.

Our results confirm that an excess of surfactant inhibits intermolecular interactions between HMHEC molecules whereas moderate amounts of surfactant strengthen them. This is seen also in the variations of the zero-shear viscosity with polymer concentration at a fixed surfactant concentration (Fig. 3). At high polymer concentrations, the addition of 9.4 mM SDS increases the viscosity of the solution appreciably, but, as the polymer concentration is reduced, the viscosity decreases much faster than that of the HMHEC solution, and eventually drops below it. For this particular SDS concentration, this happens at a polymer concentration between 4000 and 5000 ppm. An additional interesting observation of the results in Fig. 3 is that the viscosity of the HMHEC–SDS solutions decreases even below that of the HEC solutions (at a concentration between 3000 and 4000 ppm). This means that an excess of SDS not only inhibits intermolecular interactions between hydrophobic side chains, but also affects the conformation of the macromolecule. We hypothesize that this reduction is due to intramolecular cross-links in which more than one hydrophobic side chain participates in mixed micellar aggregates

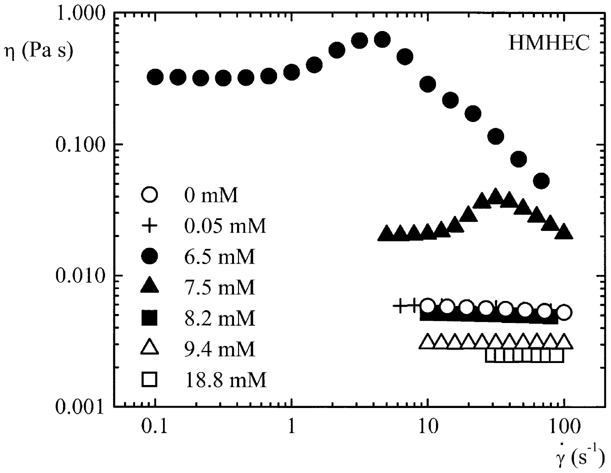

Fig. 5. Shear viscosity of solutions of 3000 ppm HMHEC and SDS. The legend indicates surfactant concentration.

with SDS. Recall that reduction in viscosity due to hydrophobes in the absence of surfactant does not occur (Fig. 3).

The effect of shear rate on the shear rheology of the 3000 and 5000 ppm HMHEC solutions is shown in Figs. 5 and 6, respectively. When the solutions have relatively low viscosities (in the absence of SDS, or at low or very high SDS concentrations), they exhibit a Newtonian or slightly shear thinning behavior. At intermediate SDS concentrations (except for 6.5 mM SDS and 5000 ppm HMHEC), the solutions have a Newtonian plateau at low shear rates, followed by a shear thickening region at intermediate shear rates, and a shear thinning region at high shear rates. This behavior is fairly typical of solutions of some associating polymers [20–22]. The shear thickening of cross-linked networks has been attributed to non-Gaussian behavior of chains stretched in the shear flow [23]. In addition, the expansion of the chains would increase the availability of sites for interaction between different coils, which leads to a higher shear viscosity. The lack of shear thickening in the 5000 ppm HMHEC with 6.5 mM SDS solution might be due to the lack of sensitivity of the viscosity to the increased level of intermolecular interactions, due to the relatively high values of the low-shear rate viscosity exhibited by this solution. Note that, when shear thickening is present, the shear rate at which shear thickening starts for each polymer solution is approximately inversely proportional to the zero-shear-rate viscosity. This indicates that the cause of the shear thickening behavior is directly related to changes in the relaxation time brought about by the interactions between the macromolecules and the solution.

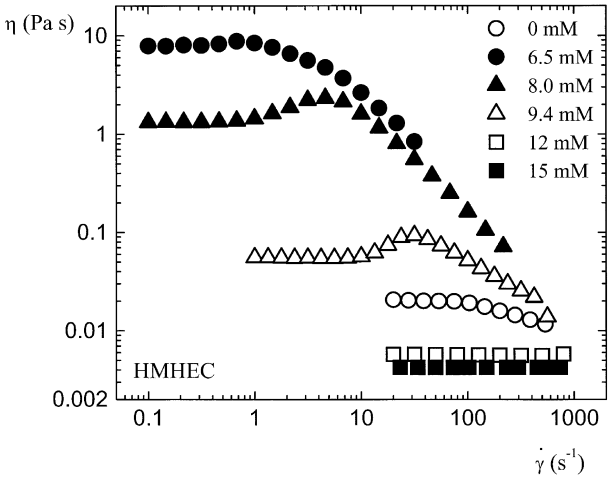

Fig. 6. Shear viscosity of solutions of 5000 ppm HMHEC and SDS. The legend indicates surfactant concentration.

From a practical standpoint, if the objective of preparing HMHEC/SDS mixtures is to increase the viscosity of the solution, results such as those shown in Figs. 5 and 6 might be used to optimize the proportions that should be used, and these proportions do not necessarily follow intuitive considerations formulated a priori. For example, comparing the shear viscosity of the solution with 3000 ppm HMHEC and 6.5 mM SDS (Fig. 5) with the solution with 5000 ppm HMHEC and 9.4 mM SDS (Fig. 6) we see that the former has a higher viscosity in most of the shear rate range explored (specifically, for shear rates below 30 s^{-1}), even though it contains less polymer and less surfactant (see also Figs. 11 and 12 and corresponding discussion). A direct comparison of these two solutions is presented and analyzed jointly with porous media flow result later in this paper (Fig. 27 and corresponding discussion).

Zero-shear viscosities of solutions of HEC2 and its modifications (cat-HEC and cat-HMHEC) are shown in Fig. 7. Note that the modified polymers have a much larger viscosity than the original polymer at low and intermediate polymer concentrations. The cationic modification confers the HEC molecule a polyelectrolytic nature. The electrostatic repulsion between cationic side groups produces a sizable expansion of the coil, which translates into higher solution viscosities, especially in the dilute regime. At high polymer concentrations, for which extensive intermolecular entanglements occur in the original polymer, the effect of

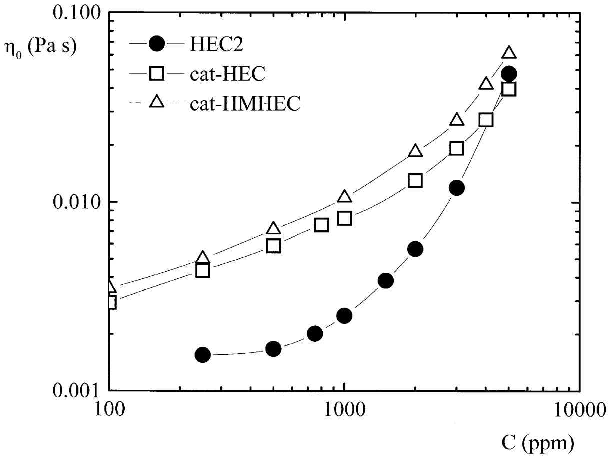

Fig. 7. Zero-shear-rate viscosity of solutions of HEC2, cat-HEC and cat-HMHEC as a function of polymer concentration.

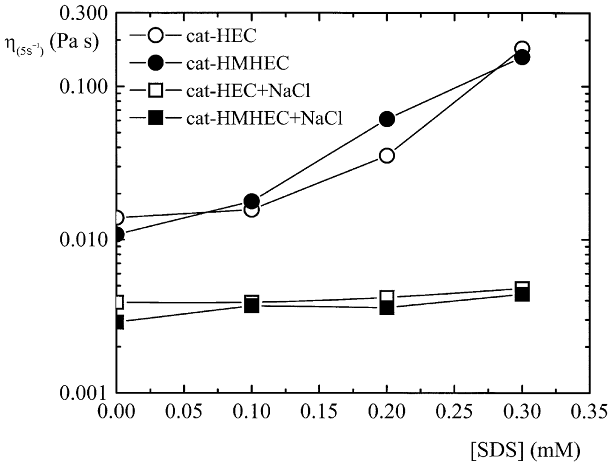

Fig. 8. Effect of SDS concentration on the shear viscosity (measured at $\dot{\gamma} = 5\ \mathrm{s}^{-1}$) of solutions of 2000 ppm cat-HEC and 1000 ppm cat-HMHEC in deionized water and 0.1 M NaCl.

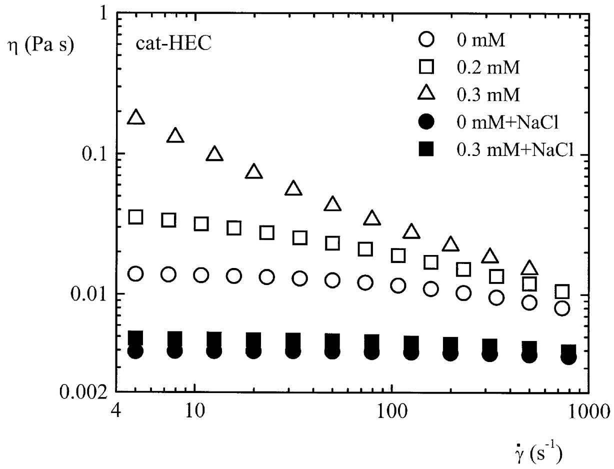

Fig. 9. Shear viscosity of solutions of 2000 ppm cat-HEC for various SDS concentrations, in deionized water and 0.1 M NaCl.

the cationic side groups on the viscosity is minimized, and the viscosity of the cat-HEC even falls slightly below that of the original HEC2 (Fig. 7). The addition of hydrophobic side groups to the cat-HEC, increases the viscosity even more, although not as dramatically as the cationic modifications, partly because of the relatively low number of hydrophobes. Note, however, that the molar substitution of the hydrophobic side chains in this case (0.007) is comparable to that of the HMHEC analyzed above (0.01).

The effect of addition of SDS to cat-HEC and cat-HMHEC solutions is shown in Fig. 8. We have selected solutions of different polymer concentrations but similar viscosity levels (1000 ppm for cat-HMHEC and 2000 ppm for cat-HEC) for this comparison. In the absence of salt, the viscosity of both polymer solutions increases substantially with SDS concentration. The increased intermolecular interactions brought about by the SDS at such low concentrations might be the result of intermolecular cross-links produced by the binding of the surfactant's hydrophilic anionic end to the cationic side chains, while the hydrophobic ends of the surfactant aggregate with other surfactant molecules attached to a different chain. This type of interaction should be easier in cat-HMHEC, since the hydrophobic side chains of this polymer might participate in interactions with hydrophobic ends of SDS molecules attached to other chains. This might explain the similarity of the behavior of cat-HEC and cat-HMHEC shown in Fig. 8 despite the difference in concentration. Note that the effect of SDS addition seems to occur even from very low SDS content. This would be incompatible with the formation of micellar aggregates that would need a critical SDS concentration to form.

The behavior of cat-HEC and cat-HMHEC as polyelectrolytes is evidenced by the results shown in Fig. 8 in the presence of 0.1 M NaCl. The chloride ions of the salt screen the cationic side groups of the polymer, thereby preventing the interactions with SDS in this range of surfactant concentration. The screening also leads to coil contraction, as evidenced by a lower viscosity level. Note that the shear viscosity of the modified polymers decreases substantially in the presence of salt. In fact, the 2000 ppm cat-HEC viscosity in the presence of NaCl is even lower than that of the unmodified polymer (Fig. 7). This might be due to intramolecular interactions between electrostatically neutralized cationic side groups.

Shear viscosities of 2000 ppm cat-HEC and 1000 ppm cat-HMHEC solutions are shown in Figs. 9 and 10 for various SDS concentrations, with and without salt. Note the pronounced shear thinning observed at higher surfactant concentrations in the absence of salt for both polymers, which is consistent with the relatively high level of intermolecular interactions. In the presence of salt, the surfactant does not have an important effect, but a certain level of increased intermolecular interactions for cat-HMHEC is hinted by the slight shear thinning observed at 0.3 mM SDS (Fig. 10).

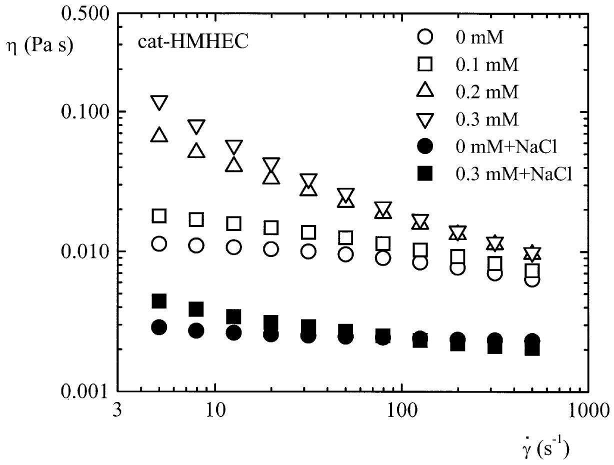

Fig. 10. Shear viscosity of solutions of 1000 ppm cat-HMHEC for various SDS concentrations, in deionized water and 0.1 M NaCl.

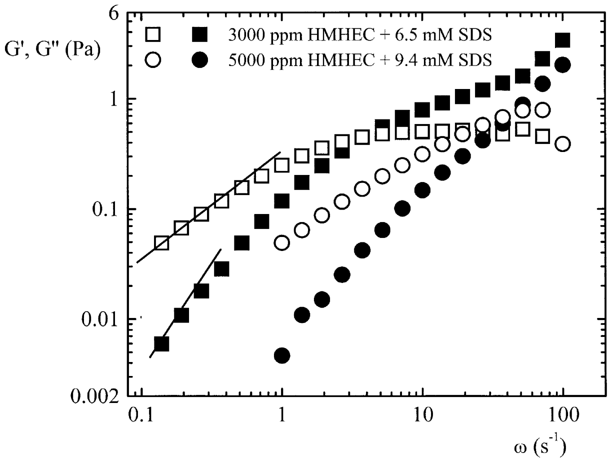

Fig. 11. Oscillatory shear behavior of two HMHEC solutions in the presence of SDS. Filled symbols represent G', open symbols represent G''. The solid lines are straight lines with slopes 1 and 2.

3.2. Shear rheology: oscillatory shear

Fig. 11 shows typical results of elastic (G') and viscous (G'') moduli for solutions of mixtures of HMHEC and SDS. At low frequencies, the G' and G'' curves approach straight lines with slopes 2 and 1, respectively, which is a common characteristic of many models that represent viscoelastic behavior, such as the Maxwell model of linear viscoelasticity. At high frequencies, the elastic modulus becomes higher than the viscous modulus. This behavior is typical of entanglements formed in polymer solutions and melts. Comparing the two solutions, we recall (Figs. 5 and 6) that the 3000 ppm HMHEC/6.5 mM SDS solution has strong intermolecular interactions due to the formation of mixed micelles, whereas the 5000 ppm HMHEC/9.4 mM SDS solution, which has a lower viscosity, contains excess surfactant and a decreased number of hydrophobic side chains in the micellar aggregates. The reduction in intermolecular effects is reflected by a substantially lower elastic and viscous moduli, as shown in Fig. 11. Fig. 12 shows comparisons between the complex viscosities obtained from the elastic and viscous moduli for the two solutions, with their simple shear viscosities. At low shear rates, both viscosities tend to coincide, as is characteristic of entangled polymer networks, but at higher shear rates, the shear thickening exhibited by the shear viscosity is not present in the complex viscosity. The fact that both viscosities are not the same in the whole range of shear rates (thus violating the Cox–Merz rule) is typical of solutions of associating polymers [24–26], and has been observed before for modified HECs [27].

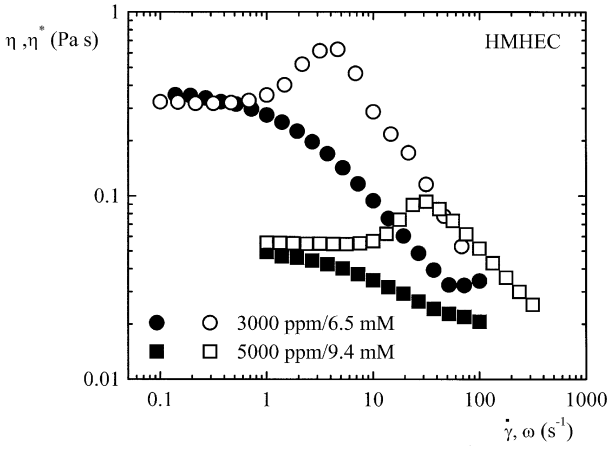

Fig. 12. Comparison between complex viscosity in oscillatory shear (filled symbols) and viscosity in simple shear (open symbols) for two HMHEC solutions in the presence of SDS.

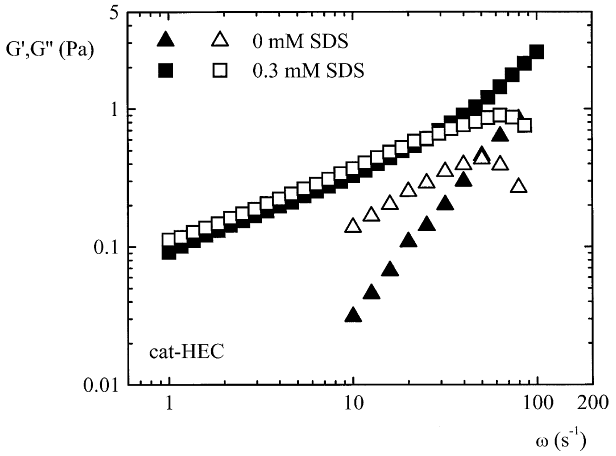

Fig. 13. Oscillatory shear behavior of 2000 ppm cat-HEC solutions, with and without SDS. Filled symbols represent G', open symbols represent G''.

Fig. 13 shows oscillatory shear behavior for solutions of cat-HEC, with and without SDS. The cat-HEC solution without surfactant exhibits the typical behavior of solutions of entangled polymers, with both moduli approaching the expected slopes at low frequencies. The cat-HEC solution with SDS, on the other hand, exhibits a much higher degree of elasticity at low frequencies, to the point that both elastic and viscous moduli have approximately the same value in a relatively wide range of frequencies. This indicates a high degree of strong intermolecular entanglements, also consistent with the high degree of shear thinning of this solution (Fig. 9). The results for cat-HMHEC are somewhat similar, as shown in Fig. 14, but, in this case, the cat-HMHEC solution with SDS has an elastic modulus that is higher than the viscous modulus in the whole range of frequencies explored.

Neither cat-HEC nor cat-HMHEC solutions satisfy the Cox–Merz rule, as shown in Fig. 15. Even though all solutions presented are shear thinning, the complex viscosity in oscillatory shear is always lower than the viscosity in simple shear flows for the solutions with SDS. In the absence of surfactant, both viscosities tend to converge at low frequencies and shear rates. Once again,

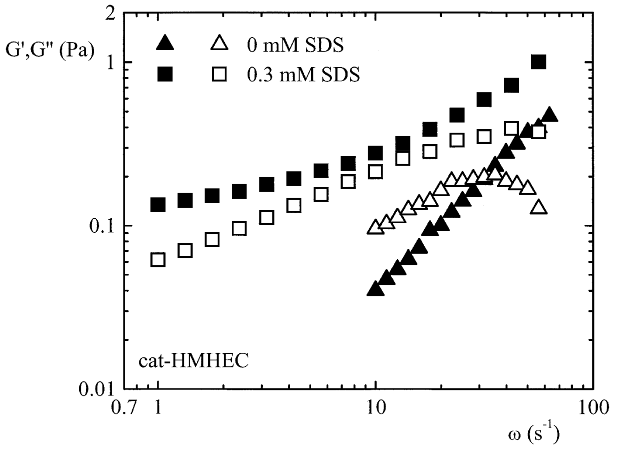

Fig. 14. Oscillatory shear behavior of 1000 ppm cat-HMHEC solutions, with and without SDS. Filled symbols represent G', open symbols represent G''.

the strong intermolecular associations induced by the cationic and hydrophobic side chains, aided by links produced by the surfactant, make these solutions depart from the typical behavior observed in entangled polymers.

3.3. Extensional rheology: flow in opposed-jets

The flow in opposed-jets represents an approximation to ideal uniaxial extension. Due to the inherent complexities of this flow, including the effect of inertia due to the curvature of the streamlines and the shear flow at the entrance of the capillaries, the measurement of pressure drops through the jets does not enable a direct determination of a true extensional viscosity [28]. However, the extension thickening behavior of polymer solutions has been widely characterized in this type of flow, and distinct parallels have been drawn between the behavior of polymer solutions in opposed-jets and in other elongational flows, such as porous media flows [14].

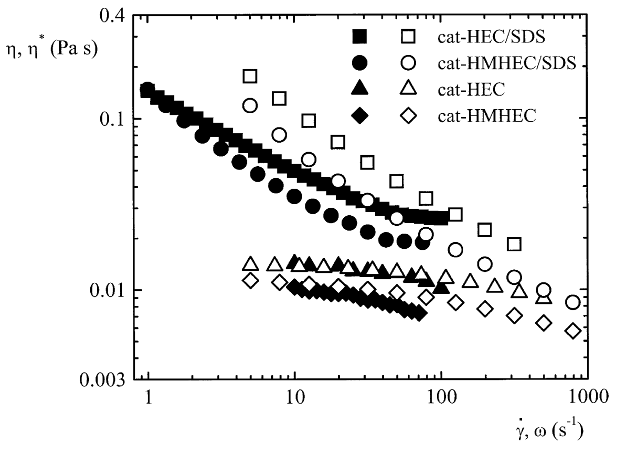

Fig. 15. Comparison between complex viscosity in oscillatory shear (filled symbols) and viscosity in simple shear (open symbols) for cat-HEC solutions (2000 ppm) and cat-HMHEC solutions (1000 ppm), with (0.3 mM) and without SDS.

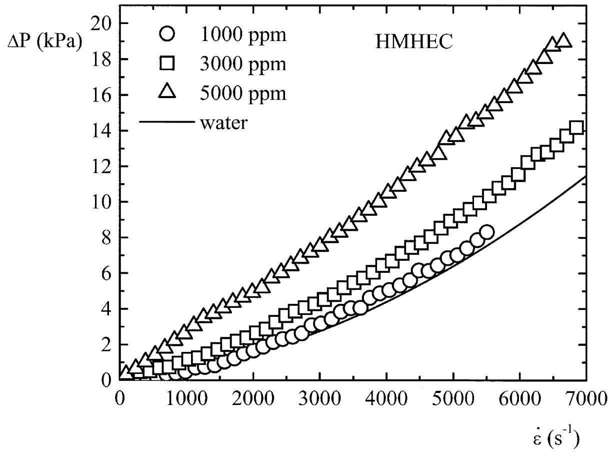

Fig. 16. Pressure drops in opposed-jets flow of HMHEC solutions of various concentrations.

Fig. 16 shows the behavior of HMHEC solutions in opposed-jets flow. At the lowest concentration (1000 ppm), the solution behaves almost like water, whereas higher concentrations lead to increased pressure drop levels. The behavior observed is typical of semi-flexible polymers in opposed-jets: while flexible polymers generally exhibit a critical extension thickening at a specific strain rate, semi-flexible polymers in the semi-dilute regime tend to behave as fluids with an increased apparent viscosity. In this regime, intermolecular entanglements occur even from the lowest strain rates, so that the pressure drop departs from the solvent's behavior from very low strain rates [14]. Solutions of HEC follow a qualitatively similar behavior to that shown in Fig. 16.

The addition of SDS to HEC solutions up to 10 mM SDS does not alter their behavior in opposed-jets flow (results not shown). However, the behavior of HMHEC is affected, as shown in Fig. 17. Note that HMHEC and HEC1 solutions without SDS exhibit similar behavior at this polymer concentration (3000 ppm) even though in simple shear

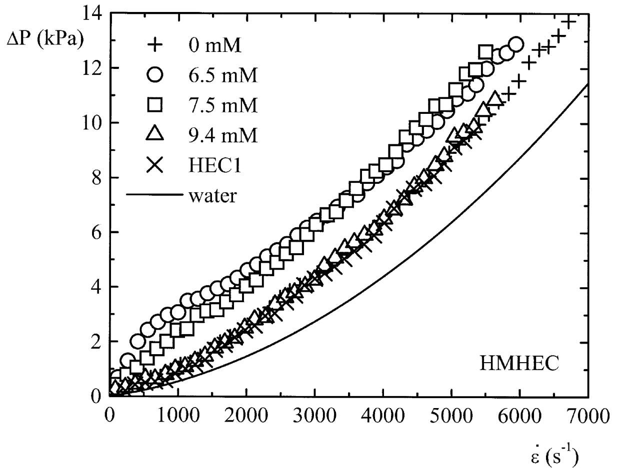

Fig. 17. Effect of SDS concentration on pressure drops of HMHEC solutions in opposed-jets flow. Results for HEC1 are shown for comparison. All solutions have a polymer concentration of 3000 ppm.

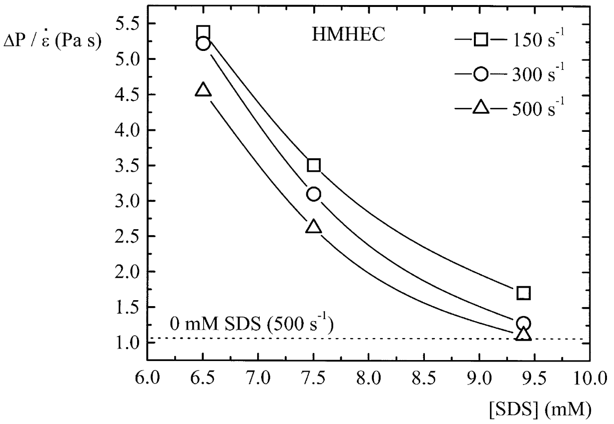

Fig. 18. Ratio of pressure drop to strain rate for 3000 ppm HMHEC solutions at low strain rates.

HMHEC solutions have a higher viscosity (Fig. 2). This might be a consequence of the reduction of effects of intermolecular interactions between hydrophobes in extensional flow: the stretching action of the flow would be capable of preventing interactions at this concentration level (see below). The addition of surfactant at concentrations of 6.5 and 7.5 mM results in increased pressure drops, which is consistent with shear viscosity results (Fig. 5), indicating that interchain interactions due to the presence of mixed micelles still control the behavior of the solutions. At higher SDS concentration (9.4 mM), the inhibition of these interactions due to electrostatic repulsion between micelles attached to hydrophobic groups lead to pressure drops similar to those of the pure polymer solution.

The ratio between pressure drop and strain rates at low strain rates gives an indication of the apparent elongational viscosity of the solutions. The effect of SDS concentration on this parameter for solutions of HMHEC is shown in Fig. 18, at three different strain rates. Note that the trend with SDS concentration is very similar to that observed for the zero-shear viscosity of these solutions (Fig. 4), with the exception that the zero-shear viscosity at 9.4 mM SDS is appreciably below that of the pure polymer, whereas the values for 9.4 mM SDS in Fig. 18 the same as those of the pure HMHEC solution (Fig. 17).

The fact that the results for HEC and HMHEC are identical indicates that the hydrophobic side chains do not play a role in the behavior of the solutions in opposed-jets flow in the absence of surfactant. A reason for this is the ‘strong’ nature of the flow due to the relatively large strain rates (compare the strain rate range in Fig. 17 with the shear rate range shown in Fig. 2), and the stretching action of the flow, which might be enough to inhibit interactions between hydrophobic side groups. However, when surfactant is added, the formation of mixed micelles between SDS molecules and hydrophobic side groups is strong enough to produce an increase in the apparent elongational viscosity of the solution thus yielding larger pressure drops (Fig. 17). On the other hand, when the amount of surfactant is large enough to inhibit interchain participation in mixed micelles (9.4 mM), the elongational viscosity of the solution does not drop below that of the solution without surfactant, as it happens with the shear viscosity, since the hydrophobic side chains do not play a role in the behavior of the solution without surfactant.

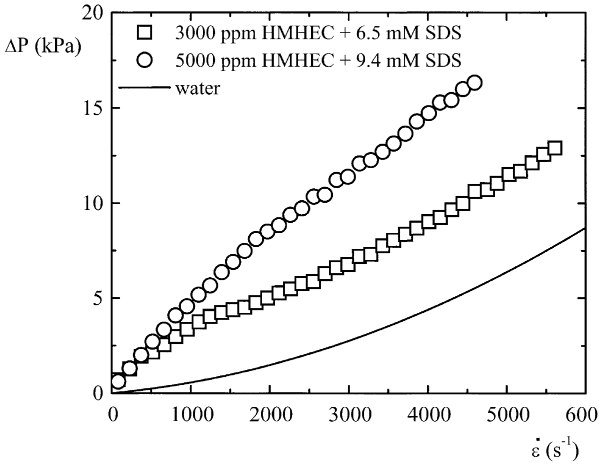

Fig. 19. Comparative behavior of two solutions of HMHEC + SDS in opposed-jets flow.

The distinct difference in behavior between shear and elongational flows is evident in the results shown in Fig. 19, which compare a 3000 ppm HMHEC + 6.5 mM SDS solution with a 5000 ppm HMHEC + 9.4 mM solution. As discussed above, the first solution has an appreciably higher shear viscosity than the second solution, even though it contains less polymers and surfactant (Figs. 5 and 6), as a consequence of the screening of hydrophobic interactions by SDS micelles in the second solution. In opposed-jets flow, Fig. 19, at low strain rates both solutions are indistinguishable while at high shear rates the pressure drop of the more concentrated solution gets to be much higher. We believe that this behavior is a consequence of the effect of the elongational flow over the coil conformation: an expansion of the coil makes intermolecular interactions more important at higher polymer concentrations due to an increased degree of chain overlap, and a reduction of interactions between hydrophobic side chains. Intramolecular temporary cross-links between hydrophobes might be broken in the elongational flow field, thus allowing the SDS to form an increased number of mixed micelles per chain in the 5000 ppm solution. This mechanism has been proposed to explain extension thickening in solutions of HASE polymers [18].

The behavior of cat-HEC solutions in opposed-jets flow, including the effect of surfactant, is shown in Fig. 20. The cat-HEC solution exhibits high-pressure drops than the unmodified polymer (HEC2) due to its ability to form stronger intermolecular entanglements induced by the coil expansion resulting from electrostatic repulsion of the

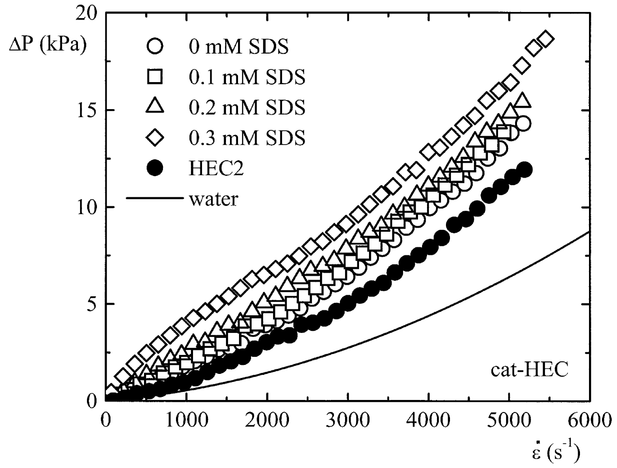

Fig. 20. Effect of SDS concentration on pressure drops of cat-HEC solutions in opposed-jets flow. Results for HEC2 are shown for comparison. All solutions have a polymer concentration of 2000 ppm.

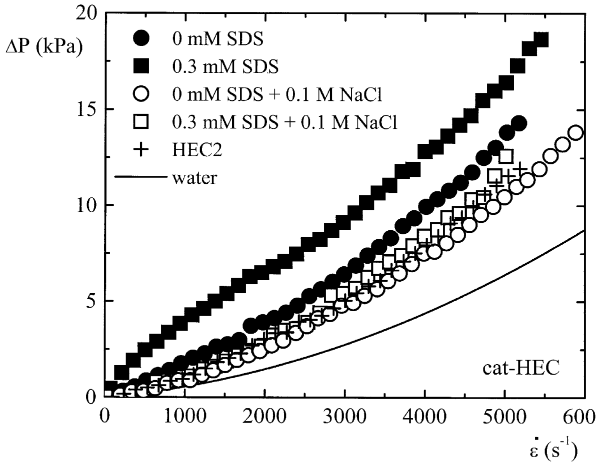

Fig. 22. Pressure drop in opposed-jets flow of cat-HEC solutions in the presence of SDS and NaCl. Results for HEC2 are shown for comparison. All solutions have a polymer concentration of 2000 ppm.

cationic groups along the chain. Addition of SDS at low concentrations induces an appreciable increase in pressure drops due to the enhancement of interchain interactions by electrostatic binding of SDS molecules to the cationic groups. These trends are similar to those observed in simple shear flows (Figs. 7 and 8). It is significant to point out that these interactions, which would be similar to interactions between hydrophobic side chains in HMHEC, are still evident in opposed-jets flow. This might be a consequence of the relatively large number of cationic sites along the cat-HEC chains.

In simple shear flow at low shear rates (Fig. 8), 1000 ppm solutions of cat-HMHEC behave very similarly to 2000 ppm solutions of cat-HEC. It was argued that this behavior was due to increased intermolecular interactions due to the added hydrophobic side chains in the HMHEC. If the extensional nature of the flow in opposed-jets is capable of disrupting these interactions, one would expect a different behavior between the 1000 ppm cat-HMHEC and the 2000 ppm cat-HEC solution in this case. The results in Fig. 21 confirm this expectation. First of all, the pressure drops for the pure cat-HMHEC solutions are only slightly higher than those of the original polymer, HEC2 (compare with the 2000 ppm solutions in Fig. 20), which reflects the reduced impact of chain extension on behavior due to the lower polymer concentration. Second, the addition of SDS does not cause an increase in pressure drop, even though it leads to higher shear viscosities (Fig. 8), since in this case the flow field is capable of preventing interactions between hydrophobes. Note that these observations are consistent with the increased elasticity (higher G') exhibited by the 2000 ppm cat-HEC solutions in oscillatory shear both with and without SDS (Fig. 13) as compared with the 1000 ppm cat-HMHEC solutions (Fig. 14).

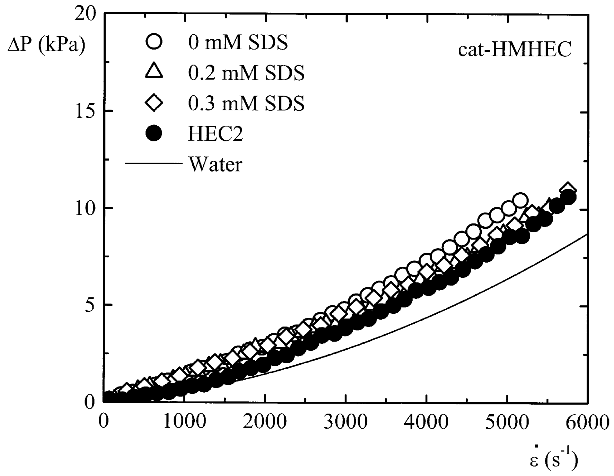

Fig. 21. Effect of SDS concentration on pressure drops of cat-HMHEC solutions in opposed-jets flow. Results for HEC2 are shown for comparison. All solutions have a polymer concentration of 1000 ppm.

The polyelectrolytic nature of the cat-HEC and cat-HMHEC polymers make them susceptible to the presence of other ionic species in solution, as revealed by the shear flow results in the presence of NaCl (Figs. 8–10). Fig. 22 shows the effect of NaCl on cat-HEC solutions. The presence of salt neutralizes the intermolecular interactions that yield increased pressure drop both in the presence and absence of surfactant. Note that the results with 0.1 M NaCl are close to those of the unmodified polymer (HEC2), although in the absence of SDS, the pressure drops seem to be slightly lower than those of the unmodified polymer. This behavior is consistent with the shear flow results.

The addition of NaCl to 1000 ppm cat-HMHEC solutions has a more dramatic effect, as shown in Fig. 23: the solution without SDS returns to levels similar to the unmodified polymer when NaCl is present, but the solution with SDS

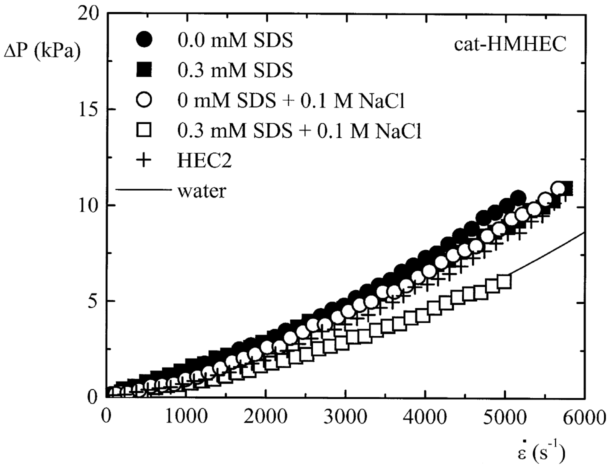

Fig. 23. Pressure drop in opposed-jets flow of cat-HMHEC solutions in the presence of SDS and NaCl. Results for HEC2 are shown for comparison. All solutions have a polymer concentration of 1000 ppm.

exhibits a much lower pressure drop, reaching levels comparable to those of water. Coil contraction due to ionic screening and the presence of intramolecular interactions between neutralized cationic groups might explain a drop in apparent viscosity below that of the original polymer, but it is not clear why this drop is much more evident in the presence of 0.3 mM SDS.

3.4. Flow in porous media

Porous media flows have important elongational components but, at the same time, there is extensive shear due to the local velocity gradients induced by the no-slip condition on the surface of the solid phase. Solutions of flexible polymers, which are shear thinning, might exhibit a strong extension thickening effect in porous media flow [14], which is more consistent with their behavior in purely elongational flows (such as opposed-jets flow) than in shear flows. In this section, we explore how some of the solutions of associative polymers employed in this work behave in this complex type of flow. The results are analyzed in terms of resistance coefficient (Eq. (2)) which can be thought of as a dimensionless apparent viscosity, since it represents the ratio of pressure drop to velocity under conditions of negligible inertia.

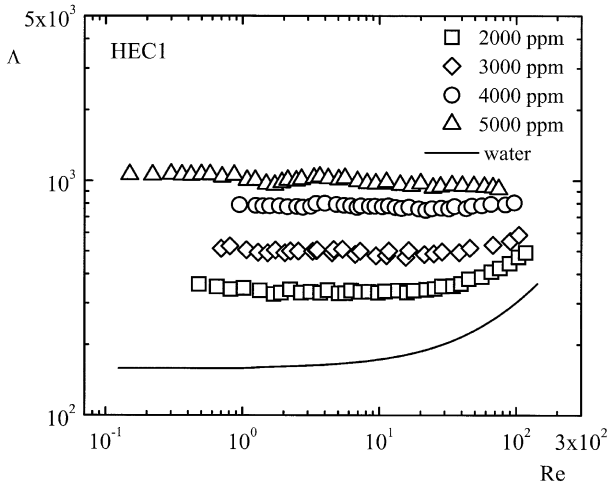

Fig. 24. Resistance coefficients of HEC1 solutions in flow through porous media. The legend indicates polymer concentration.

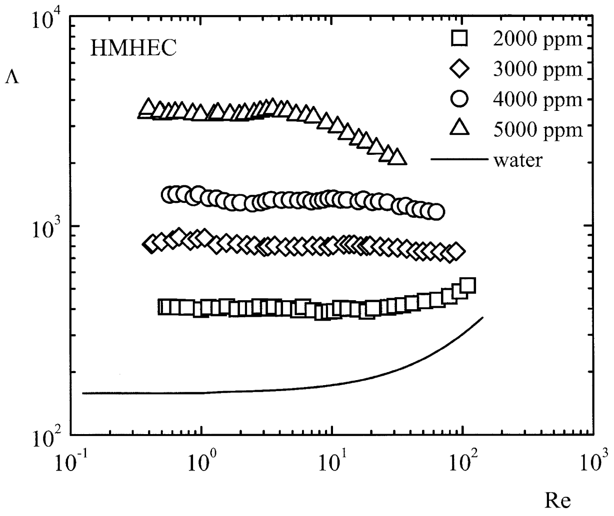

Fig. 25. Resistance coefficients of HMHEC solutions in flow through porous media. The legend indicates polymer concentration.

Fig. 24 shows the porous media flow results for HEC1 solutions. The solutions behave as Newtonian fluids (constant resistance coefficient, except for the 2000 and 3000 ppm solution at the highest Re, due to the onset of inertial effects in the flow). These results reflect exactly the behavior of the solutions in shear flow (Fig. 2). In fact, the ratio of resistance coefficients for any two concentrations coincides with the ratio of shear viscosities. The same correspondence is observed for HMHEC (Fig. 25): low concentration solutions behave as Newtonian fluids in the whole range of Reynolds number, whereas shear thinning sets in at high polymer concentration, following shear viscosity trends (Fig. 2).

The direct correspondence between shear and porous media flow is demonstrated by considering two solutions as specific examples: 5000 ppm HMHEC + 9.4 mM SDS and 3000 ppm HMHEC + 6.5 mM SDS. The porous media flow results for these solutions, along with the solutions in the absence of surfactant, are shown in Fig. 26. If shear flow dominates the behavior of these solutions in porous media, then we can postulate that Λ is proportional to the shear viscosity, η. According to this we can calculate an apparent viscosity for the porous media flow results, based on the measured value of Λ/Λ_w, where Λ_w is the resistance coefficient for water at low Reynolds number, since the viscosity of water is known. The correspondence between

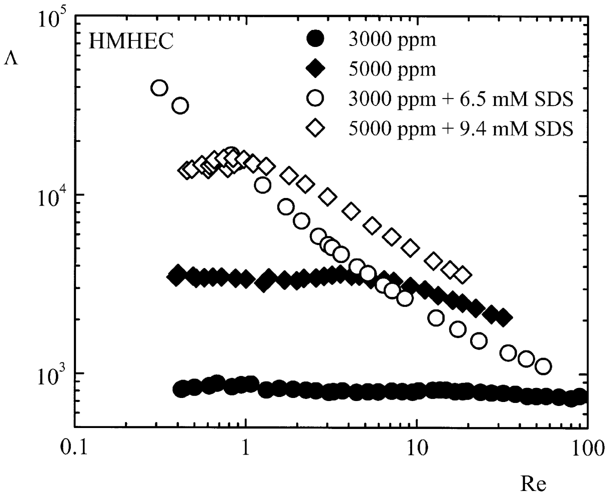

Fig. 26. Comparative behavior of two HMHEC solutions in porous media flow with and without SDS.

shear rate and Reynolds number (or superficial velocity) is not so clear, but we can postulate that the local shear rate in the porous medium is given by

$$\dot{\gamma} = \frac{v}{\phi \ell} \tag{4}$$

where v/ϕ is the interstitial velocity of the fluid, and ℓ is a characteristic length. We have used ℓ as a single adjustable parameter to try to superimpose the curves of apparent viscosity calculated from the porous media flow results with the shear viscosity curves. The results are shown in Fig. 27, corresponding to $\ell = 0.04d$. The almost perfect match proves that the behavior of these solutions in porous media flow is dominated by the shear component of the flow. This correspondence indicates that these polymers have a negligible degree of flexibility under the conditions analyzed, since extension thickening effects are not evident in porous media flows. Similarly, solutions of cat-HEC and cat-HMHEC in porous media flows also follow the same trend exhibited by the shear viscosity, as shown in Fig. 28. In this case, the characteristic length that provided overlap was $\ell = 0.06d$.

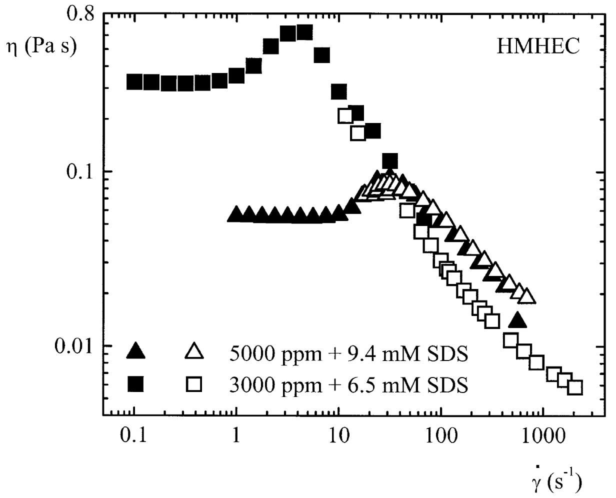

Fig. 27. Superposition of shear viscosity data (filled symbols) with apparent viscosities calculated from porous media flow results (open symbols) for two HMHEC + SDS solutions using the procedure outlined in the text.

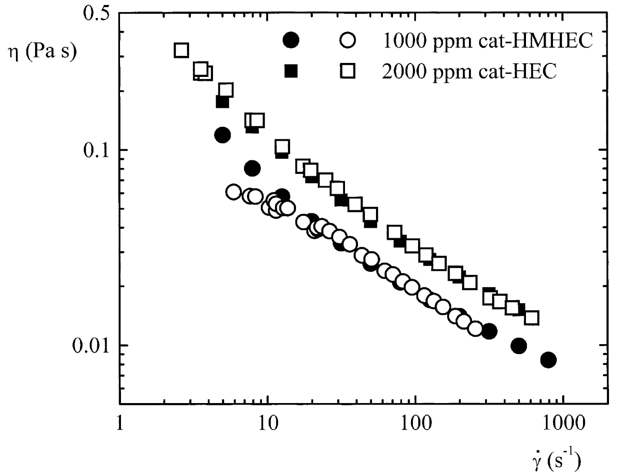

Fig. 28. Superposition of shear viscosity data (filled symbols) with apparent viscosities calculated from porous media flow results (open symbols) for cat-HEC and cat-HMHEC solutions with 0.3 mM SDS.

4. Conclusions

The presence of hydrophobic grafts along the HEC chain induces intermolecular interactions that lead to an increased shear viscosity with higher levels of shear thinning. These interactions are strengthened in the presence of SDS to the point that the solution separates into two phases. At relatively high surfactant concentrations, a single-phase with a relatively high viscosity is obtained, due to strengthening of intermolecular interactions by the formation of mixed micelles containing hydrophobes from different chains. These solutions exhibited a degree of shear thickening in a range of shear rates. At even higher surfactant contents, the reduction of the number of hydrophobes in the mixed micelles leads to shear viscosity reduction to levels even lower than those of the original polymer, due to the inhibition of interactions between hydrophobes caused by electrostatic repulsions between the SDS micelles. The interactions between hydrophobes in the absence of surfactant did not affect pressure drops measured in opposed-jets flow, which might seem to indicate that the strong extensional nature of the flow is capable of disrupting this type of interactions. Upon the addition of SDS, the formation of mixed micelles did induce an increase in the apparent elongational viscosity of the solution. Clearly, the mixed micelles formed between SDS and hydrophobic side chains in the polymer are stronger than interactions between hydrophobes.

The cationic side groups confer a polyelectrolytic nature to the HEC. They expand the polymer coil, resulting in higher shear viscosities and higher apparent extensional viscosities. The addition of SDS to the cat-HEC strengthens interchain interactions even at very low surfactant concentrations. This effect is explained in terms of interchain bridging by surfactant molecules whose hydrophilic end interacts with the cationic side groups while the hydrophobic ends interact with surfactant molecules attached to different polymer molecules. The polyelectrolytic nature of cat-HEC also is demonstrated by a strong inhibition of intermolecular interactions in the presence of relatively high concentrations of NaCl as revealed by both shear and extensional rheology.

The addition of hydrophobic side groups to cat-HEC further increases intermolecular interactions in shear flows, but they have no appreciable effect in opposed-jets flow, due to inhibition of hydrophobe interactions.

In the range of conditions studied, porous media flow results with HEC and its modifications follow the same trend as the shear viscosities, indicating that the shear nature of the flow dominates over its extensional nature.

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