Available online at www.sciencedirect.com
SCIENCE @ DIRECT®
ELSEVIER
Polymer 44 (2003) 6965–6971
polymer
www.elsevier.com/locate/polymer

Viscous pressure behaviour in shear-induced concentration banding

M. Criado-Sancho[a,*], D. Jou[b,c], J. Casas-Vázquez[b]

[a]*Departamento de Ciencias y Técnicas Fisicoquímicas, UNED, Senda del Rey 9, 28040 Madrid, Spain*
[b]*Departament de Física, Universitat Autònoma de Barcelona, 08193 Bellaterra, Catalonia, Spain*
[c]*Institut d'Estudis Catalans, Carme 47, 08001 Barcelona, Catalonia, Spain*

Received 12 February 2003; received in revised form 30 April 2003; accepted 12 May 2003

Abstract

The behaviour of the viscous pressure as a function of the shear rate is studied for a non-Newtonian polymer solution in a cone-and-plate device, in the presence of a shear-induced concentration banding transition. In this transition, where the system splits into two bands with different polymer concentrations, the slope of the viscous pressure is shown to have a clear discontinuity. This behaviour is rather different from the one observed in shear banding in liquid crystals, where concentration remains homogeneous but the system splits into two bands with different orientations and shear rates.

Keywords: Polymer solutions; Concentration banding; Chemical potential

1. Introduction

Polymer solutions and blends, as well as suspensions and colloids, exhibit interesting couplings between diffusion and viscous pressure when submitted to a shear flow, leading, for instance, to modifications in the phase diagram, and to shear-induced diffusion [1–9]. In this general context, we have studied the concentration banding in polymer solutions in shear flow [10,11]. In this phenomenon, a polymer solution initially homogeneous, and which would remain homogeneous at rest, splits into several regions or bands with different values of the polymer concentration, provided the value of the shear stress is higher than some threshold. For values of the shear stress lower than the threshold, the concentration is mildly inhomogeneous, with a smooth variation of the concentration profile rather than with some differentiated regions separated by steep variations of the concentration.

In Refs. [10,11], we proposed a simple thermodynamic model for concentration banding in several flow geometries (cone-and-plate flow and Poisueille flow along a tube). We started from the evolution equations for the concentration, velocity and viscous pressure tensor and studied their stability. In particular, in the constitutive equation for the diffusion flux, it appears a non-equilibrium chemical potential dependent on the flow, given by the sum of the local-equilibrium chemical potential plus some corrections dependent on the local viscous pressure. These non-equilibrium contributions may change the stability domain of the solution with respect to the one predicted by the stability analysis using the local-equilibrium theory [4,10,11], thus leading, under some conditions, to the mentioned concentration shear banding, which may be considered, in fact, as a non-equilibrium phase transition.

The aim of this paper is to study a new aspect of this transition which up to our knowledge has not yet been analysed in the literature, namely, the modification in the apparent or effective viscosity of the solution when banding appears. This aspect has experimental and practical interest: indeed, the change in the viscosity provides an experimental method to detect the phase transition at increasing values of the shear rate and, on the other side, it influences the flow conditions in industrial processing of polymer solutions. Another original aspect of this paper is that we take explicitly into account non-Newtonian effects which had been ignored in the previous calculations, where linear viscoelastic behaviour was assumed. The paper is distributed in two sections: Section 2 introduces explicitly the definition of the effective viscosity and it presents the essential ideas of the thermodynamic description of the shear banding; in Section 3, the pertinent calculations for

---

[*] Corresponding author.

0032-3861/03/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0032-3861(03)00618-9

the present purposes are carried out. Section 4 is devoted to a discussion of the results.

2. Thermodynamic model of shear-induced concentration banding

To be concrete, we will consider the cone-and-plate flow geometry, for which more data are available than for other geometries. A polymer solution is introduced into the device. At rest, the solution is homogeneous. When the cone rotates slowly, at a fixed angular speed, it appears a shear-induced diffusion of the polymer towards the central region of the device, in such a way that the concentration profile decreases smoothly from the higher value near the apex to lower values near the walls [10,12–14]. At a threshold value of the rotation rate, the concentration profile is no longer smooth, but a steep separation between two different zones is observed. This difference in concentrations becomes steeper and steeper for increasing values of the rotation rate. In previous papers, we studied the mentioned changes in the concentration profile. Here, our aim is to study the variation of the apparent shear viscosity during the separation process.

The essential idea is that the constitutive equation for the diffusion flux $\mathbf{J}$ is [4,10]

$$\mathbf{J} = -\tilde{D}\nabla\mu - \frac{D}{RT}\nabla\cdot\mathbf{P}^{\mathrm{v}} \tag{2.1}$$

with μ the non-equilibrium chemical potential of the solute, $\mathbf{P}^{\mathrm{v}}$ the viscous pressure tensor, D the classical diffusion coefficient and $\tilde{D}$ a transport coefficient related to D through the relation $D = \tilde{D}(\partial\mu_{\mathrm{eq}}/\partial n)^{-1}$, with n the solute concentration (in moles per unit volume). The second term in this equation describes a coupling between viscous pressure and diffusion. To describe the evolution of concentration, the constitutive Eq. (2.1) must be complemented with an equation of state for the chemical potential. Introduction in Eq. (2.1) of the generalised chemical potential yields

$$\mathbf{J} = -D_{\mathrm{eff}}\nabla c - \frac{D}{RT}\nabla\cdot\mathbf{P}^{\mathrm{v}} \tag{2.2}$$

where D_{eff} is an effective diffusion coefficient defined by [13]

$$D_{\mathrm{eff}} = \frac{D}{(\partial\mu_{\mathrm{eq}}/\partial n)}\left(\frac{\partial\mu}{\partial n}\right) \tag{2.3}$$

The use of a generalized non-equilibrium chemical potential dependent on the flow and different from the local-equilibrium chemical potential has two main motivations. First, the experimental observation [12] that the separation rate predicted from Eq. (2.1) with the local-equilibrium chemical potential is much lower than the observed one, whereas it becomes much enhanced when a suitable form of non-equilibrium chemical potential is used [13]. Second, from a microscopic point of view it is clear that the flow stretches and orientates the macromolecules, thus modifying their free energy with respect to the quiescent situation. The latter comment suggests that the modifications of the chemical potential are expected to be very small in dilute suspensions of spherical rigid particles, which are not deformed nor oriented by the flow. For this reason, the contribution of the divergence of the viscous pressure tensor to the diffusion flux is found both in polymer solutions [1–6] as in suspensions [7–9], whereas the non-equilibrium contributions to the chemical potential are more typical of the former. For concentrated suspensions, however, the possible relevance of the effects of the flow, which could contribute to some ordering of the particles in layers, has not yet been studied, up to our knowledge.

For values of the shear rate higher than a threshold, $D_{\mathrm{eff}}(c,\dot{\gamma})$ becomes negative between two values of the concentration $c_1(\dot{\gamma})$ and $c_2(\dot{\gamma})$. In general lines, our proposal was that for such values of the shear rate the system splits into two band of concentrations $c_1(\dot{\gamma})$ and $c_2(\dot{\gamma})$. To determine the values of $c_1(\dot{\gamma})$ and $c_2(\dot{\gamma})$ an expression for the non-equilibrium chemical potential is needed. This was explicitly obtained in Ref. [10], where the dependence of $c_1(\dot{\gamma})$ and $c_2(\dot{\gamma})$ on the molecular mass of the polymer was also taken into account, leading to the possibility of practical applications in shear-induced mass separation.

Assume that the system splits into two concentration bands, and internal one with concentration $c_1(\dot{\gamma})$ and radius r_1 and an external one, with concentration $c_2(\dot{\gamma})$, between the radius r_1 and the external radius R, under an homogeneous and fixed shear rate $\dot{\gamma}$ proportional to the rotation rate. Then, the average shear stress $P^{\mathrm{v}}_{\phi\theta}$ on the circular basis of the cone-and-plate device may be evaluated as

$$P^{\mathrm{v}}_{\phi\theta} = \frac{\eta_1\pi r_1^2 + \eta_2\pi(R^2 - r_1^2)}{\pi R^2}\dot{\gamma} \equiv \eta_{\mathrm{eff}}(\dot{\gamma})\dot{\gamma} \tag{2.4}$$

Here, η_1 and η_2 refer, respectively, to the values of the viscosity in the two bands, which depends on the respective polymer concentration. Furthermore, r_1 is determined by the mass conservation law when $c_1(\dot{\gamma})$ and $c_2(\dot{\gamma})$ are determined as a function of the shear rate. When the system is homogeneous the viscosity is η_0.

The change in the viscosity near the critical value of the shear rate where the transition appears does not require, in principle, new arguments beyond those presented in Ref. [10] for the evaluation of $c_1(\dot{\gamma})$ and $c_2(\dot{\gamma})$. However, we will go farther from them in order to take into account some non-Newtonian aspects neglected in Refs. [10,11], and we will take into account that the viscosity of the homogeneous solution changes as a function of the shear rate, for high enough values of the shear rate, in accordance with the experimental information.

3. Explicit calculation of the values of concentration in the two bands

In this section we will compute explicitly $c_1(\dot{\gamma})$ and $c_2(\dot{\gamma})$. In contrast with the calculations already presented in Ref. [10] we will introduce non-Newtonian effects neglected there, i.e. the dependence of the viscosity of the solution on the shear rate, which is needed for high enough values of the shear rate. This Section is rather technical and may be skipped in a first reading. The results are presented and discussed in detail in Section 4.

3.1. Flow contributions to the Gibbs free energy

First of all, let us recall the main ideas of our thermodynamic model for the banding transition. From the model of EIT, it is known that the non-equilibrium contribution to the Gibbs free energy for a macromolecular solution under a viscous pressure $\mathbf{P}^{\mathrm{v}}$ is given by [4,10,14,15]

$$G^{(s)} = \frac{1}{4} v_1 \Omega J \mathbf{P}^{\mathrm{v}} : \mathbf{P}^{\mathrm{v}} \tag{3.1}$$

where v_1 is the molar volume of the solvent, $\mathbf{P}^{\mathrm{v}}$ the viscous pressure tensor, J the steady state compliance and $\Omega = n_1 + m n_2$ is a well-known quantity in the lattice model when one considers a system with n_1 moles of solvent and n_2 moles of polymer, m being the degree of polymerization of the macromolecules.

When the Rouse–Zimm model is applied, and is it is assumed that the viscosity depends on the concentration according to

$$\frac{\eta_0(\tilde{c})}{\eta_{\mathrm{s}}} = 1 + \tilde{c} + k\tilde{c}^2 \tag{3.2}$$

η_{s} being the solvent viscosity, k Martin's constant, η_0 the viscosity assuming Newtonian behaviour and $\tilde{c}$ the reduced concentration defined as $\tilde{c} = [\eta]_0 c$ being $[\eta]_0$ the intrinsic viscosity of the Newtonian system, it is possible to rewrite the non-equilibrium contribution (3.1) as

$$G^{(s)} = \frac{1}{4} C \frac{v_1 M_2 [\eta]_0}{RT} \Omega \Phi(\tilde{c}) \mathbf{P}^{\mathrm{v}} : \mathbf{P}^{\mathrm{v}} \tag{3.3}$$

where C is a constant whose value is 0.4 for the Rouse model, M_2 the solute molecular mass and $\Phi(\tilde{c})$ a function of the reduced concentration $\tilde{c}$ whose explicit expression is given in Ref. [4].

In the particular case of a cone-and-plate configuration, the tensorial product $\mathbf{P}^{\mathrm{v}} : \mathbf{P}^{\mathrm{v}}$ takes the explicit form

$$\mathbf{P}^{\mathrm{v}} : \mathbf{P}^{\mathrm{v}} = \left(\frac{RT}{M_2 [\eta]_0} \right)^2 \tilde{c}^2 [4(\lambda\dot{\gamma})^4 + 2(\lambda\dot{\gamma})^2] \tag{3.4}$$

where λ is the viscoelastic relaxation time.

In our previous analyses, it was assumed a viscoelastic Newtonian behaviour. Here we will go beyond this model and we will introduce some non-Newtonian effects. Thus, the viscosity will be assumed to depend not only on the concentration but also on the shear rate, in such a way that Eq. (3.2) will be generalized as

$$\frac{\eta(\tilde{c}, \dot{\gamma})}{\eta_{\mathrm{s}}} = 1 + \hat{f}_1(\dot{\gamma})\tilde{c} + \hat{f}_2(\dot{\gamma})\tilde{c}^2 \tag{3.5}$$

where $\hat{f}_1$ and $\hat{f}_2$ are function of the shear rate whose explicit form will be discussed below. Thus, instead the function $\Phi(\tilde{c})$ appearing in Eq. (3.3) the new function $\hat{\Phi}(\tilde{c})$ defined as

$$\hat{\Phi}(\tilde{c}, \dot{\gamma}) = \tilde{c} \left(\frac{\hat{f}_1 + \hat{f}_2 \tilde{c}}{1 + \hat{f}_1 \tilde{c} + \hat{f}_2 \tilde{c}^2} \right)^2 \tag{3.6}$$

must be used.

Furthermore, it will be assumed that the time constant λ depends on the concentration, namely $\lambda = \lambda(\tilde{c})$.

3.2. Non-equilibrium chemical potential

Following the proposals in Ref. [10], the chemical potential is considered as the sum of two terms, the equilibrium one, corresponding to the Flory–Huggins model, and another one, obtained from the non-equilibrium contribution to the Gibbs free energy. Thus, the polymer chemical potential is given by

$$\mu_2 = \mu_2^{(\mathrm{FH})} + \left(\frac{\partial G^{(s)}}{\partial n_2} \right)_{T,p,n_1,\mathbf{P}^{\mathrm{v}}} \tag{3.7}$$

Thus, after introduction of Eq. (3.6) into (3.3) and subsequent differentiation, one obtains from Eq. (3.7)

$$\mu_2 = \mu_2^{(\mathrm{FH})} + \frac{1}{4} C \frac{v_1 M_2 [\eta]_0}{RT} \mathbf{P}^{\mathrm{v}} : \mathbf{P}^{\mathrm{v}} m \left[\hat{\Phi} + \tilde{c} \frac{1-\phi}{\phi} \left(\frac{\partial \hat{\Phi}}{\partial \tilde{c}} \right)_{\mathbf{P}^{\mathrm{v}}} \right] \tag{3.8}$$

where ϕ is the polymer volume fraction. Note that the requirement of constant $\mathbf{P}^{\mathrm{v}}$ during the differentiation, together with Eq. (3.4) and the dependence $\lambda = \lambda(\tilde{c})$ indicates that there exists a functional relation $\dot{\gamma} = \dot{\gamma}(\tilde{c})$ which must be taken into account during the differentiation in Eq. (3.7). After some algebraic manipulations, it is possible to write

$$\left(\frac{\partial \hat{\Phi}}{\partial \tilde{c}} \right)_{\mathbf{P}^{\mathrm{v}}} = \frac{1}{\tilde{c}} \left(\hat{\Phi} + 2 \frac{\hat{P}_5}{\hat{P}_6} \right) + 2 \frac{\hat{P}_3}{\hat{P}_6} \frac{1}{\dot{\gamma}} \left(\frac{\partial \dot{\gamma}}{\partial \tilde{c}} \right)_{\mathbf{P}^{\mathrm{v}}} \tag{3.9}$$

where the following polynomials of the reduced concentration have been defined

$$\begin{aligned} \hat{P}_5 &= (\hat{f}_1 \hat{f}_2 - \hat{f}_1^3)\tilde{c}^2 + (\hat{f}_2^2 - 3\hat{f}_1^2 \hat{f}_2)\tilde{c}^3 - 3\hat{f}_1 \hat{f}_2^2 \tilde{c}^4 - \hat{f}_2^3 \tilde{c}^5, \\ \hat{P}_6 &= (1 + \hat{f}_1 \tilde{c} + \hat{f}_2 \tilde{c}^2)^3, \\ \hat{P}_3 &= \hat{f}_1 \hat{f}_1{}' \tilde{c} + (\hat{f}_1 \hat{f}_2{}' + \hat{f}_2 \hat{f}_1{}')\tilde{c}^2 + \hat{f}_2 \hat{f}_2{}' \tilde{c}^3 \end{aligned} \tag{3.10}$$

where there appear the derivatives $\hat{f}_i' \equiv \partial \hat{f}_i'/\partial \ln \dot{\gamma}$ $(i = 1, 2)$. Note that the first two polynomials are a generalization of those that have been used in our previous works [10].

In order to compute the derivatives of the shear rate with respect to the concentration, we write the Deborah number $x = \lambda\dot{\gamma}$, in terms of which it is possible to write

$$\frac{1}{\dot{\gamma}}\left(\frac{\partial\dot{\gamma}}{\partial\tilde{c}}\right)_{\mathbf{P}^{\mathrm{v}}} = \frac{1}{x}\left(\frac{\partial x}{\partial\tilde{c}}\right)_{\mathbf{P}^{\mathrm{v}}} - \frac{1}{\lambda}\frac{\mathrm{d}\lambda}{\mathrm{d}\tilde{c}} = -\frac{1}{\tilde{c}}\hat{Q}(\dot{\gamma},\tilde{c}) \qquad (3.11)$$

where the derivative of x with respect to the concentration is obtained immediately from Eq. (3.4). However, the derivative of the relaxation time and, therefore, the explicit expression of $\hat{Q}(\dot{\gamma},\tilde{c})$ requires the knowledge of $\hat{f}_1(\dot{\gamma})$ and $\hat{f}_2(\dot{\gamma})$.

In terms of $\hat{Q}(\dot{\gamma},\tilde{c})$ the chemical potential of the polymer is given by

$$\frac{\mu_2}{RT} = \frac{\mu_2^{(\mathrm{FH})}}{RT} + C\tilde{c}[2(\lambda\dot{\gamma})^4 + (\lambda\dot{\gamma})^2] \times\left(\frac{\hat{\Phi}}{2} + (1-\phi)\frac{\hat{P}_5 - \hat{P}_3\hat{Q}}{\hat{P}_6}\right) \qquad (3.12)$$

3.3. Dependence of the viscosity on concentration and shear rate

An accurate description of the observed effect requires to takes into account Non-newtonian effects for high enough values of the shear rate; indeed, for many polymer solutions there is shear thinning, i.e. a reduction of the viscosity with increasing values of the shear rate, for high values of $\dot{\gamma}$; we propose for the shear-dependent viscosity the expression

$$\begin{aligned} &\eta(\dot{\gamma},\tilde{c}) = \eta_0(\tilde{c}) \qquad (\dot{\gamma} < \dot{\gamma}_0) \\ &\eta(\dot{\gamma},\tilde{c}) = B_1(\tilde{c})\dot{\gamma}^{B_2(\tilde{c})} \qquad (\dot{\gamma} \geq \dot{\gamma}_0) \end{aligned} \qquad (3.13)$$

where B_1 and B_2 are functions of $\tilde{c}$, given by

$$B_1(\tilde{c}) = b_{10} + b_{11}\tilde{c} + b_{12}\tilde{c}^2, \qquad B_2(\tilde{c}) = b_{20} + b_{21}\tilde{c} \quad (3.14)$$

since for all values of $\dot{\gamma}$ (Eq. (3.13) must predict the solvent viscosity η_s when $\tilde{c} = 0$, the joint expression (3.13) and (3.14) leads to the conclusion that $b_{20} = 0$ and $b_{10} = \eta_\mathrm{s}$. Furthermore, when this result is taken into account in the definition of intrinsic viscosity, one may write

$$\begin{aligned} \frac{[\eta]}{[\eta]_0} &= \lim_{\tilde{c}\to 0}\frac{1}{\tilde{c}}\left[\frac{\eta(\dot{\gamma},c)}{\eta_\mathrm{s}} - 1\right] \\ &= \lim_{\tilde{c}\to 0}\frac{1}{\tilde{c}}[(1 + \bar{b}_{11}\tilde{c} + \bar{b}_{12}\tilde{c}^2)\dot{\gamma}^{b_{21}\tilde{c}} - 1] \end{aligned} \qquad (3.15)$$

where the subindex 0 stands for the Newtonian situation and where the new parameters $\bar{b}_{11} = b_{11}/\eta_\mathrm{s}$ and $\bar{b}_{12} = b_{12}/\eta_\mathrm{s}$ have been introduced. After application of the L'Hopital rule it is concluded that

$$\frac{[\eta]}{[\eta]_0} = \bar{b}_{11} + b_{21}\ln\dot{\gamma} \qquad (3.16)$$

this agrees with the results of Kotaka et al. [16] also recorded by Bird et al. [17, p. 107]. From these references it may be estimated that $\bar{b}_{11} = 1.649$ and $b_{21} = 0.0669$. According with the modelization of viscosity given by Eq. (3.13) the intersection of Eq. (3.16) with the horizontal line $[\eta]/[\eta]_0 = 1$ gives us an upper limit value of $\dot{\gamma}$ for which the Newtonian behaviour may be assumed. It follows from the quoted values of $\bar{b}_{11}$ and b_{21} and by equating (3.16) to 1 that this upper value of $\dot{\gamma}$ in the limit of vanishing polymer concentration is given by $\dot{\gamma} \cong 1.6 \times 10^4\ \mathrm{s}^{-1}$.

If the exponential appearing in Eq. (3.13) is expanded up to the second order in $\tilde{c}$, one arrives to expression (3.6) with the functions $\hat{f}_1$ and $\hat{f}_2$ given by

$$\begin{aligned} &\hat{f}_1(\dot{\gamma}) = \bar{b}_{11} + b_{21}\ln\dot{\gamma}, \\ &\hat{f}_2(\dot{\gamma}) = \bar{b}_{12} + \bar{b}_{11}b_{21}\ln\dot{\gamma} + \frac{1}{2}(b_{21}\ln\dot{\gamma})^2 \end{aligned} \qquad (3.17)$$

up to this point, all the parameters appearing in Eq. (3.14) have been determined, at the exception of b_{12}, and the comparison of Eqs. (3.2) and (3.5) will allow us to study its influence on the results. To do this, we introduce the new parameter α defined as $\bar{b}_{12} = \alpha k$. In Fig. 1, the curves represent values of η/η_s predicted from Eq. (3.5) for several values of α and the reduced concentrations. When substituting each of the considered values of $\tilde{c}$ in Eq. (3.2) one obtains the horizontal lines plotted in the Figure, whose intersection with the curves determines the shear rate $\dot{\gamma}_0$ beyond which the behaviour of the system cannot be considered as Newtonian. If it is accepted that non-Newtonian effects increase for increasing values of the concentration, it seems logical to conclude that this behaviour must begin for values of $\dot{\gamma}$ lower than $1.60 \times 10^4\ \mathrm{s}^{-1}$ previously derived by the arguments explained below Eq. (3.16). This gives an estimation of the acceptable values of α. Thus, for $\tilde{c} = 1$, Fig. 2 indicates that the value of α

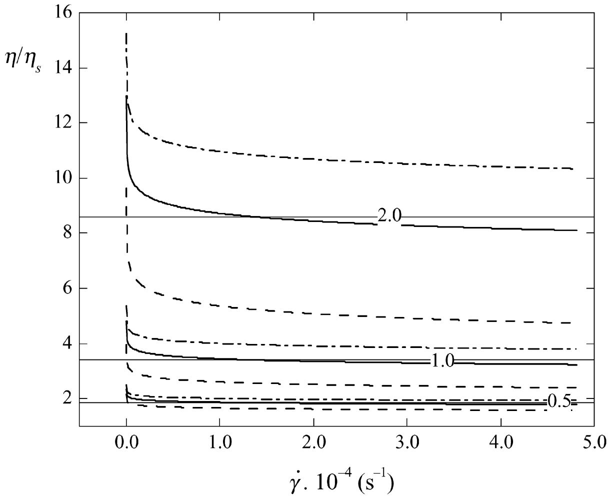

Fig. 1. Dependence on $\dot{\gamma}$ of the quantity η/η_s calculated from Eq. (3.5) using $\alpha = 1.0$ (dashed curve), $\alpha = 1.6$ (continuous curve) and $\alpha = 2.0$ (dot and dashed curve). Every set corresponds to the reduced concentration values shown in the figure. The horizontal lines are the plot of η/η_s assuming Newtonian behaviour and the composition dependence given by Eq. (3.2).

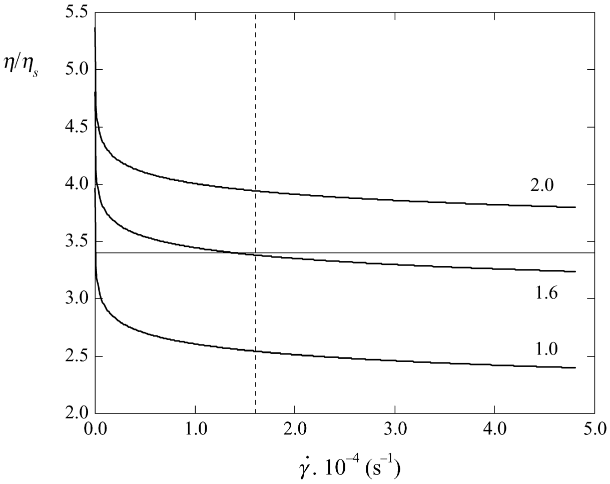

Fig. 2. Plot of η/η_s obtained from Eqs. (3.2) and (3.5) when $\tilde{c} = 1.0$ and the parameter α takes the values indicated in the figure. The vertical line corresponds to the upper shear rate limit for which Newtonian behaviour can be assumed, namely $1.6 \times 10^4\ s^{-1}$, as explained in the text. Thus, the values of α of the order of 1.6 seem preferable, as they give the intersection with the horizontal line in the required position. For lower values of $\dot{\gamma}$, we take for η/η_s the value corresponding to the horizontal line.

must be of the order of 1.6. On the other side, it must be noted that the intersection point between Eqs. (3.2) and (3.5) for a given concentration is obtained by solving a simple algebraic equation and this allows to define the function $\gamma_0(\tilde{c})$ which indicates the maximum value of $\dot{\gamma}$ for which the system behaves as Newtonian at a given concentration. Furthermore, [17, p. 228], when expression (3.13) is adopted for the viscosity, the corresponding time constant is given by $\lambda = 1/\dot{\gamma}_0$ and, according to which has been pointed out above, the change of the time constant as a function of concentration for different values of α is plotted in Fig. 3. Note that for the value $\alpha = 1.6$ selected from the arguments given in Fig. 2, the concentration dependence of λ is much less pronounced than for values of α of 1.5 and 1.7. Furthermore, since for increasing $\tilde{c}$ the value of λ is expected to increase, it seems that the value $\alpha = 1.7$ and higher ones are not satisfactory because they yield an opposite behaviour.

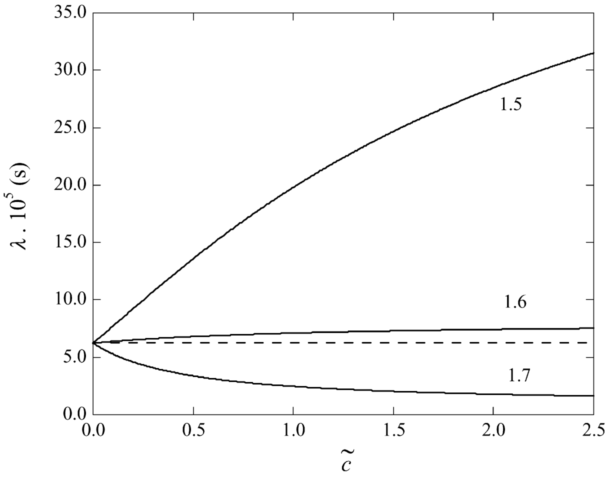

Fig. 3. Viscolastic relaxation time vs. concentration for several values of α. The dashed line corresponds to the inverse of the upper shear rate limit for which Newtonian behaviour can be assumed.

From Eqs. (3.4), (3.11), and (3.17) one arrives at the result

$$\hat{Q}(\dot{\gamma},\tilde{c}) = \frac{2(\lambda\dot{\gamma})^2+1}{4(\lambda\dot{\gamma})^2+1} + \frac{\tilde{c}}{b_{21}} \times \frac{0.5(b_{21}\ln\lambda)^2 - \bar{b}_{11}b_{21}\ln\lambda + (\alpha-1)k}{1+\bar{b}_{11}\tilde{c} - b_{21}\tilde{c}\ln\lambda} \quad (3.18)$$

which allows us to have an explicit expression for the chemical potential.

4. Results: concentration banding and viscous pressure as a function of the shear rate

Once the non-equilibrium chemical potential is known, one may obtain the form of the effective diffusion coefficient (2.3), which is proportional to the derivative of the chemical potential at constant shear rate. To obtain explicit results, we will use for the several coefficients the data reported for a solution of polystyrene in transdecalin which we have used in some of our previous papers [4].

The derivative of the chemical potential has been computed numerically, and the results for the boundaries of the stability region, in the Deborah-number vs. the shear rate diagram, are plotted in Fig. 4 in the Newtonian and non-Newtonian situations. In Fig. 5 it is plotted the shear rate as a function of concentration, which yields $c_1(\dot{\gamma})$ and $c_2(\dot{\gamma})$ as the intersections of the boundary curve with the horizontal line corresponding to a given shear rate. The minimum of the curve corresponds to the threshold value of the shear rate at which banding begins. In Fig. 5 it is seen that the

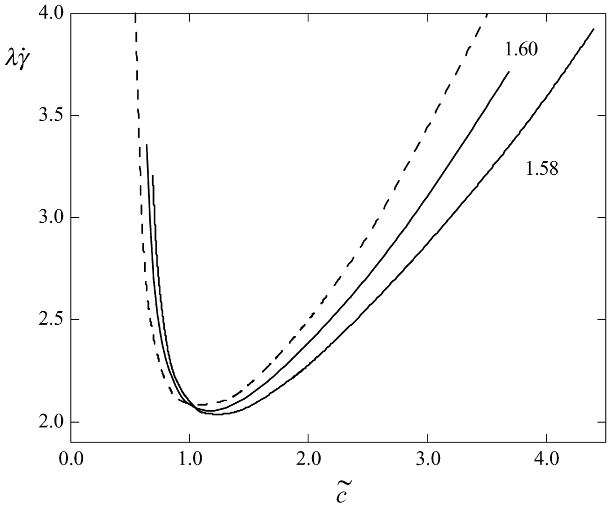

Fig. 4. Deborah number and concentration for which the effective diffusion coefficient is zero. The dashed curve corresponds to Newtonian behaviour. The continuous curves are calculated for non-Newtonian behaviour using the values of α indicated in the figure.

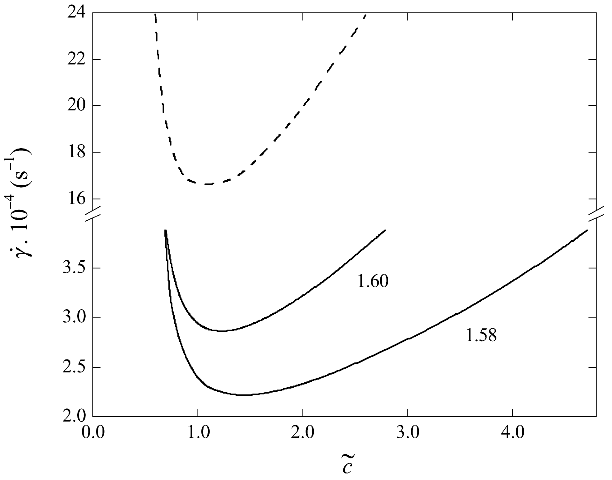

Fig. 5. Shear vs. reduced concentration when the effective diffusion coefficient is zero. The dashed curve corresponds to Newtonian behaviour. The continuous curves are calculated for non-Newtonian behaviour using the values of α indicated in the figure. The minimum of the curves yield the critical value of $\dot{\gamma}$ at which banding begins.

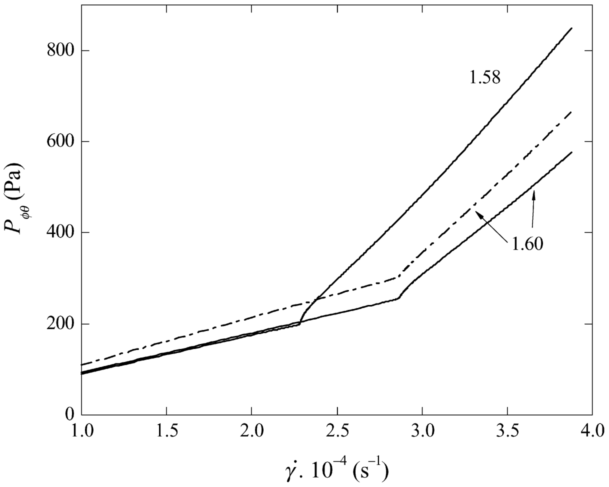

Fig. 6. Viscous pressure as a function of shear rate when $\tilde{c}_0 = 1.1$ (continuous curves) and $\tilde{c}_0 = 1.3$ (dot and dashed curve) using the values of α indicated in the figure. Note the marked change of slope at the shear rate corresponding to the beginning of the banding transition.

introduction of non-Newtonian effects implies important modifications with respect to the previous situation, and which are mainly due to the concentration dependence of the time constant. Note that for decreasing values of the parameter α, there is a reduction of the critical value for the shear rate. Thus, a more sensitive experimental evaluation of α could be obtained from the position of the critical value of $\dot{\gamma}$.

Once the values of $c_1(\dot{\gamma})$ and $c_2(\dot{\gamma})$ have been obtained, the value of the radius r_1 corresponding to the boundary between both bands is determined by the mass balance condition, which imposes that

$$\tilde{c}_0 R^3 = \tilde{c}_1 r_1^3 + \tilde{c}_2 (R^3 - r_1^3) \tag{4.1}$$

where $\tilde{c}_0$ is the homogeneous concentration in the system at rest.

Now, the values of $c_1(\dot{\gamma})$, $c_2(\dot{\gamma})$, r_1, $\eta_1(\tilde{c}, \dot{\gamma})$ and $\eta_2(\tilde{c}, \dot{\gamma})$ are known. By introducing them into Eq. (2.4), the total value of $P^{\mathrm{v}}_{\phi\theta}$ may be computed. In Fig. 6 the results for $P^{\mathrm{v}}_{\phi\theta}$ as a function of $\dot{\gamma}$ are plotted for several values of α and $\tilde{c}_0$. It is seen that the slope of $P^{\mathrm{v}}_{\phi\theta}$ shows a sudden change for the value of $\dot{\gamma}$ corresponding to the banding transition. This change could be used to detect the phase transition from measurements of the viscous pressure in terms of $\dot{\gamma}$, instead that detecting it from direct measurements of the density for different values of the radius.

5. Concluding remarks

We have studied the behaviour of the viscous pressure of a polymer solution near the concentration banding transition in a cone-and-plate device. The slope of the viscous pressure as a function of the shear rate shows a sudden increase at the transition. This increase is due to the fact that the viscosity of the solution increases with the polymer concentration, in such a way that the effect of the appearance of a band with high concentration predominates over the effect of the decrease of the viscosity in the band with decreasing concentration.

This behaviour is rather different from the one described in the literature for another, different banding transition, namely, shear banding in liquid crystals or rigid rods between two rotating cylinders [18–22]. In this case, the concentration remains homogeneous but not the orientation. The system splits into two bands, one nematic and another isotropic, with different values of the shear rate but the same value of the viscous pressure. In the transition, a sudden change of slope of the viscous pressure as a function of the shear rate is observed, similarly to what happens in our case. The differences are that the slope decreases instead of increasing, as it is observed in our study. This is due to the fact that the oriented molecules of the nematic phase appearing in the banding transition exhibit a smaller viscosity than the original isotropic phase found in the system at rest or for small values of the shear rate. This is in contrast with our problem, where the new phase has a higher viscosity than the original system. Thus the difference of behaviours may be understood rather intuitively.

In the mentioned situations of rigid rods, the behaviour of the viscous pressure as a function of the shear rate is non-monotonous, in such a way that there is a region where a horizontal line corresponding to a given value of $\mathbf{P}^{\mathrm{v}}$ intersect three times the curve. In this case, the values $\dot{\gamma}_1$ and $\dot{\gamma}_2$ of the shear rate of each band are the highest and the lowest values of $\dot{\gamma}$, whereas the value of $\dot{\gamma}$ at the intermediate intersection corresponds to an unstable regime.

Another difference of our work with respect to that of Olmsted et al. [18,19] is that they obtain two sudden changes of slope: one at the shear rate where the banding initiates and another one for the shear rate where the whole system is in the nematic phase, in such a way that no bands are longer found but the system is homogeneous again (but nematic instead of isotropic). In contrast, we have only studied the behaviour when banding initiates, but not the saturation situation where the concentration of the inner band has arrived at a maximum value. Indeed, we do not have reliable data on this saturation behaviour, which would correspond to a situation where all macromolecules overlap. If a behaviour of this kind was considered, the slope of the viscous pressure is expected to have a sudden change there, since no further changes in the internal structure of the system would happen.

Acknowledgements

We acknowledge the financial support of the Dirección General de Investigación Científica y Técnica of the Spanish Ministry of Science and Technology under grant BFM2000-0351-003-0 and the Direcció General de Recerca of the Generalitat of Catalonia under contract 2001-SGR-000186.

References

[1] Agarwal US, Dutta A, Mashelkar RA. Chem Engng Sci 1994;49: 1693.
[2] Onuki A. J Phys: Condens Matter 1997;9:6119.
[3] Onuki A. Phase transitions dynamics. Cambridge: Cambridge University Press; 2002.
[4] Jou D, Casas-Vázquez J, Criado-Sancho M. Thermodynamics of fluids under flow. Berlin: Springer; 2000.
[5] Wolf BA. Macromolecules 1984;17:615.
[6] Rangel-Nafaile CA, Metzner A, Wissbrun K. Macromolecules 1984; 17:1187.
[7] Nott PR, Brady JF. J Fluid Mech 1994;275:157.
[8] Mills P, Snabre P. J Phys II France 1995;5:1597.
[9] Morris JF, Boulay F. J Rheol 1999;43:1213.
[10] Jou D, Criado-Sancho M, del Castillo LF, Casas-Vázquez J. Polymer 2001;42:6239.
[11] Jou D, Criado-Sancho M, Casas-Vázquez J. Polymer 2002;43:1599.
[12] MacDonald MJ, Muller SJ. J Rheol 1994;40:259.
[13] Del Castillo LF, Criado-Sancho M, Jou D. Polymer 2000;41:2633.
[14] Jou D, Casas-Vázquez J, Lebon G. Extended irreversible thermodynamics, 3rd ed. Berlin: Springer; 2001.
[15] Jou D, Casas-Vázquez J, Lebon G. Rep Prog Phys 1988;51:1105. Jou D, Casas-Vázquez J, Lebon G. Rep Prog Phys 1999;62:1035.
[16] Kotaka T, Suzuki H, Inagaki H. J Chem Phys 1966;45:2770.
[17] Bird RB, Armstrong RC, Hassager O. Dynamics of polymeric liquids. New York: Wiley; 1987.
[18] Olmsted PD, Lu CYD. Phys Rev E 1999;60:4397.
[19] Olmsted PD. Europhys Lett 1999;48:339.
[20] Fisher E, Callaghan PT. Phys Rev E 2001;64:011501.
[21] Goveas JL, Fredickson GH. J Rheol 1999;43:1261.
[22] Yuan XF. Europhys Lett 1999;46:542.