

Entropic effects on the rheological behaviour of *n*-eicosane and comparison with *n*-heptadecane

Roberto C. Dante^{a*}, Enrique Geffroy-Aguilar^a and A.E. Chávez^b

^aDepartment of Rheology, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior S/N, Ciudad Universitaria, Coyoacán, Mexico City 04510, Mexico; ^bDepartment of Chemical Engineering, Universidad Nacional Autónoma de México, Facultad de Química Conjunto E, Circuito de la Investigación Científica S/N, Coyoacán, Mexico City 04510, Mexico

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Alkanes are among the main components of crude oil, and heptadecane and eicosane are often among those with alkanes of average molar fraction. It is known that their rheological behaviour is directly related to the micro-phases these compounds can form. Their shear steady viscosity follows the pattern of a shear thinning region with a subsequent plateau. However, mixtures rich in eicosane or pure eicosane exhibit a viscosity increment with temperature at low shear rates, briefly named ‘temperature thickening’ in this study. This unusual behaviour can be explained through the formation of ordered structures, probably similar to those of liquid crystals, at low temperatures near the melting point, which disappear at higher temperatures provoking a significant entropy arising.

Keywords: alkanes; rheology; entropy production; non-equilibrium thermodynamics; alkanes’ phases

1. Introduction

Crude oil rheology frequently shows a shear thinning behaviour in steady shear strain conditions as well as normal stresses, as described in several papers [1–10]. This complex behaviour depends partially on the aliphatic fraction. This article focusses on steady shear viscosity of heptadecane and eicosane, which are included frequently among the compounds of the aliphatic fraction of crude oil, with the average number of carbon atoms. Depending on the temperature of the mixture, these alkanes are part of both the paraffinic fraction and the colloidal or suspended fractions of crude oils and these can be found in a liquid or a solid phase, or in the so-called rotator phase [7]. Therefore, comprehension and knowledge of their rheological properties can clarify and enlighten many aspects of crude oil’s rheology. The normal alkanes exhibit a rich polymorphic nature, which depends on the number *n* of carbon atoms in the molecule and *the parity of n*, besides temperature and pressure. Pairs of *n*-alkanes with a small difference in chain length ($\Delta n = 1$ or 2) readily mix in the solid state, i.e. show a mixed-crystal formation. Moreover, it is generally observed that forms, which make their appearance for pure *n*-alkanes from

*Corresponding author. Email: rcdante@yahoo.com

a certain value of n are stabilised in binary systems at considerably lower values of n . From this observation, it is clear that the temperature *versus* composition phase diagram of a binary system may have a complex structure depending on n and Δn . In the solid phase, even alkanes, such as eicosane, have a triclinic T_p form up to a number of carbon atoms of 26, while odd alkanes, such as heptadecane, present a dimorphism, crystallising either as an orthorhombic form O_i or in the so-called rotator phase R_I [7]. In the rotator forms, the molecules have various kinds of rotational freedom, which are characterised by oscillations around the long axis.

These thermodynamic phase changes, determined by means of differential scanning calorimetry (DSC) techniques, are briefly presented and commented. The rheology of crude oil is widely discussed in several papers and readers are referred to these studies [8–12]. However, the complexity of crude oil cannot be reduced completely to the physics and rheology of linear alkanes, but the latter compound mixtures work adequately, at least, for modelling viscous properties, and to explain some non-Newtonian properties, such as normal stresses of Mexican crude oils [8–10].

This study is especially focussed on discussing the phenomenon of the increment of viscosity with increasing temperature observed for both eicosane and mixtures of heptadecane with high content of eicosane. This phenomenon is linked to the entropy accumulated from melting temperature to the experiment temperature, which seems to oppose the ordering effect of the applied shear strain.

2. Methodology and experiments

The rheological tests were carried out by a strain-controlled rheometer called advanced rheometric expansion system (ARES). The same cone-plate geometry was used for all tests with an angle of 0.04 rad and a plate radius of 50 mm. By means of a calorimeter of thermal analysis (TA) Instruments, model 2910, DSC measurements were carried out to determine the phase change temperatures of pure alkanes n -heptadecane (C17), n -eicosane (C20) and their mixtures.

3. Results

3.1. DSC experimental results

The DSC results are resumed in Figure 1, where phase change temperatures of C20, C17 and those of some mixtures are shown. In Figure 1, the dimorphism of the odd C17 is present in the mixtures of alkanes. The transition to the liquid phase occurs at higher temperatures, and involves all the degrees of freedom for the molecules. According to other measurements [7], at the extreme left of the Figure 1, the solid phase transitions to the rotator phase R_I should occur from an orthorhombic phase O_i . Moving to the right side, there is monoclinic form, and then the orthorhombic O_p , which are all typical forms of odd- n alkanes. To the extreme right of the phase diagram, the transition to the rotator phase R_I takes place from a triclinic T_p structure, typical of even- n alkanes.

The point marked with a triangle may correspond to a phase transition, from orthorhombic forms, typical of odd alkanes, to the triclinic form typical of even alkanes. Since this phase transition is restrained to very high fractions of the even

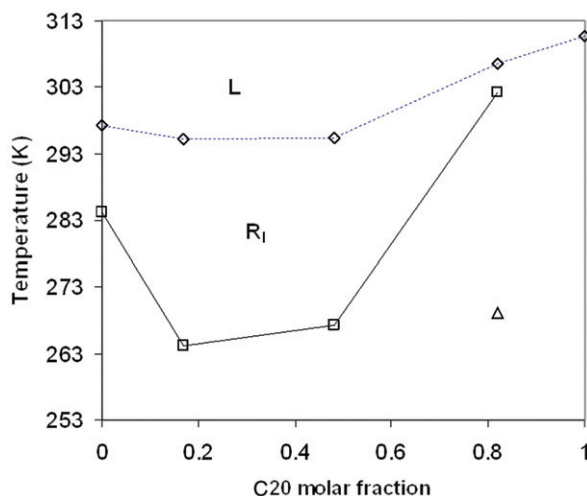


Figure 1. Phase change temperature diagram for mixtures of *n*-eicosane C20 and *n*-heptadecane C17. Notes: L is the liquid phase and R_I the rotator phase. Beneath the square symbols (\square) there are the different forms of solid phases, which are not specified for the shortage of points. The triangle symbol (\triangle) represents another solid–solid phase transition, which occurs at high eicosane molar fractions.

alkanes, no more points belonging to this transition are shown in Figure 1. The rotator phase R_I dominates between the C20 molar fraction of 0.2–0.6 and the temperature range of 263–298 K. Nevertheless, in such alkanes the presence of a well-defined upper liquid phase with a certain degree of order cannot be excluded.

3.2. Rheological results

The steady shear viscosity for C17, at four different temperature levels above the melting point of 297 K, is shown in Figure 2. These four curves are very close to each other. The shear thinning region is very large and only, at high shear rates, around 10 s^{-1} , the Newtonian region begins. For the case of C20, although test temperatures are higher than the melting point (about 311 K), a dispersion of curves is observed clearly, instead of a group of close curves as in the former case. The rheological measurements show two groups of viscosity: one for higher temperatures 345–355 K, and characterised by higher viscosities with a more pronounced shear thinning behaviour, and then the group of viscosities in the range of 315–325 K (Figure 3). However, at the end of the shear thinning region, the remaining Newtonian viscosity of the lower temperature group is higher than that of the higher temperature group. The viscosity values are similar for low temperatures in both the cases, but in general, at low shear rates, the viscosities of C20 are higher than those of C17.

The curves of the first coefficient of normal stresses Ψ_1 of C20 and C17, are shown in Figure 4(a) and (b), respectively. Eicosane's Ψ_1 curves tend to follow a tighter group behaviour than that observed for the viscosities' curves, while heptadecane curves show a certain dispersion without a clear trend dependent on

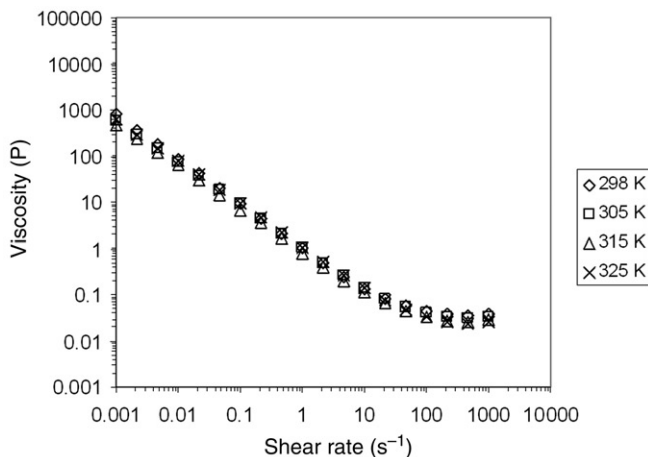


Figure 2. Steady shear viscosity for *n*-heptadecane C17, at different temperatures.

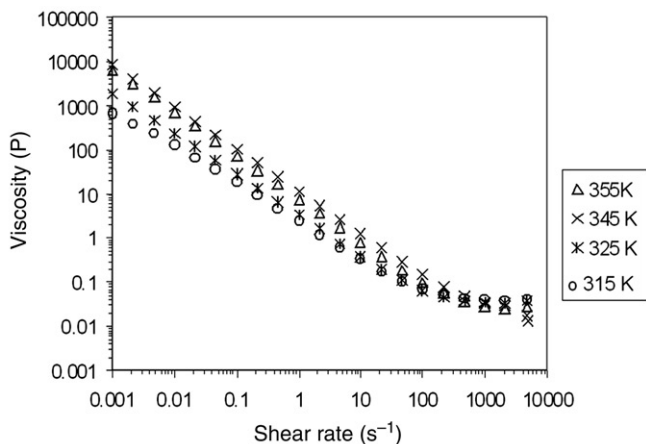


Figure 3. Steady viscosity for *n*-eicosane at different temperatures.

temperature. Also, the shear thinning region is longer than in the case of the viscosity curves, and no Newtonian plateau is observed, but only a slight change of slope. It is noteworthy to mention that for eicosane the Ψ_1 curve, at 355 K, especially at low shear rates, has values lower than the other Ψ_1 curves.

The mixture of molar fraction of 0.82 presents rheological characteristics similar to those of pure eicosane (Figure 5); although, in general, viscosities are lower, but there is not a clear correspondence between the viscosity level and temperature.

In the case of the mixture of molar fraction of 0.17 (Figure 6), the viscosity curves are very similar in shape and magnitude to those of pure heptadecane, but they are split at high shear rates in an evident manner.

Finally, it is noteworthy to indicate that the transient viscosities of C20 at 315 K and those of C17 at 305 K have a completely different evolution. Indeed, C20

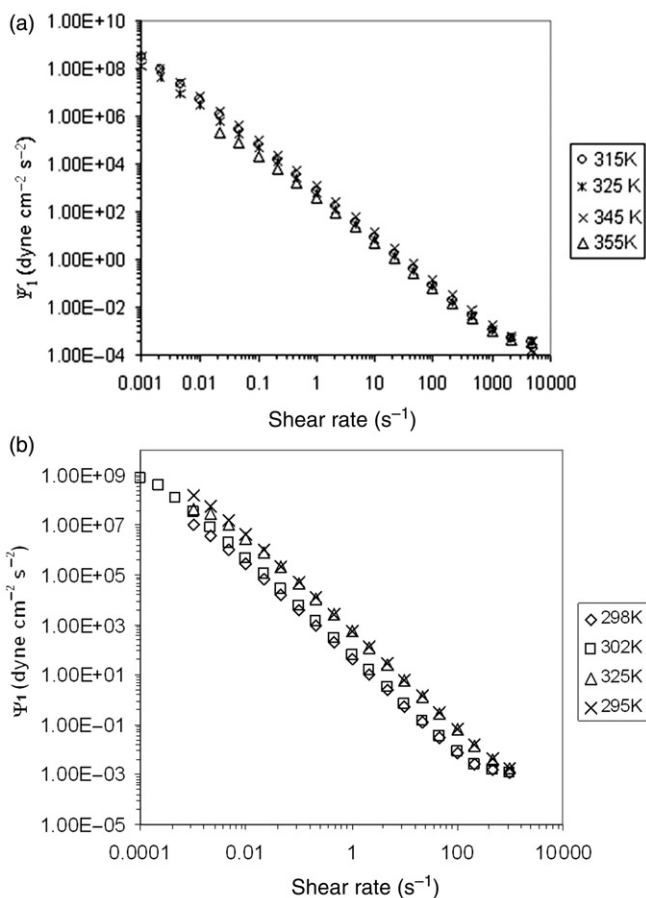


Figure 4. The first coefficient of normal stresses Ψ_1 , at different temperatures: (a) *n*-eicosane and (b) *n*-heptadecane.

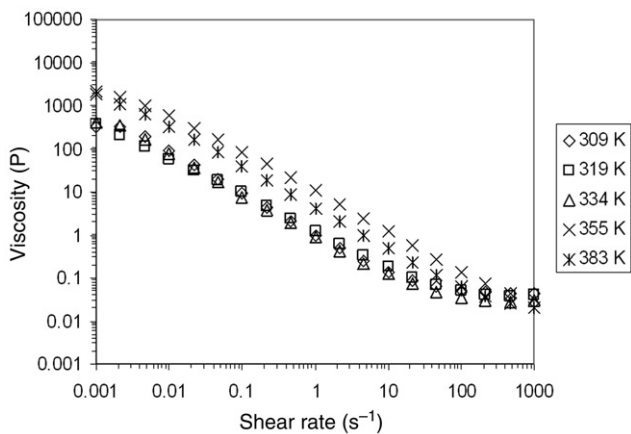


Figure 5. Steady viscosity of the mixtures of *n*-eicosane C20 and *n*-heptadecane C17, the C20 molar fraction is 0.82.

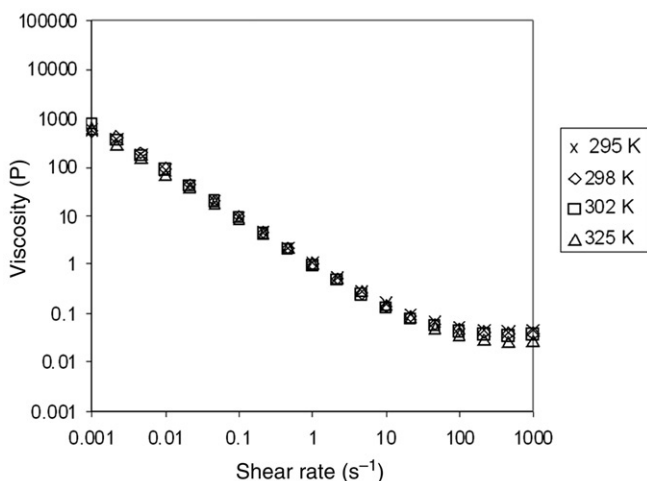


Figure 6. Steady viscosity of the mixtures of *n*-eicosane C20 and *n*-heptadecane C17, the C20 molar fraction is 0.17.

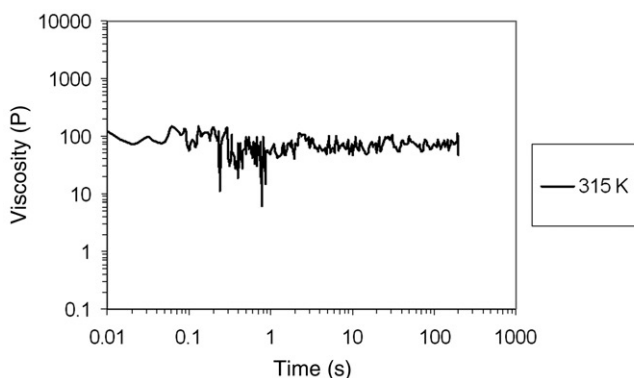


Figure 7. Transient viscosity for *n*-eicosane C20 at the shear rate of 10^{-2}s^{-1} and at a temperature of 315 K.

Note: The time interval between a measure and following one is 0.01 s.

(Figure 7) reaches the steady state quicker and with fewer oscillations than C17 (Figure 8). The transient tests were carried out at the same shear rate of 10^{-2}s^{-1} for both alkanes: for C20 at a temperature about 4 K more than its melting point, and for C17 at about 4 and 11 K more than its melting point, respectively.

4. Discussion

The mixtures of C17 and C20 inherit part of the properties of both alkanes, e.g. the rotator phase is quite dominant in the mixtures (Figure 1), while the transition point from the solid form to the rotator phase rises with incrementing fractions of C20. Above the melting temperature, the alkane in excess quantity seems to dominate the

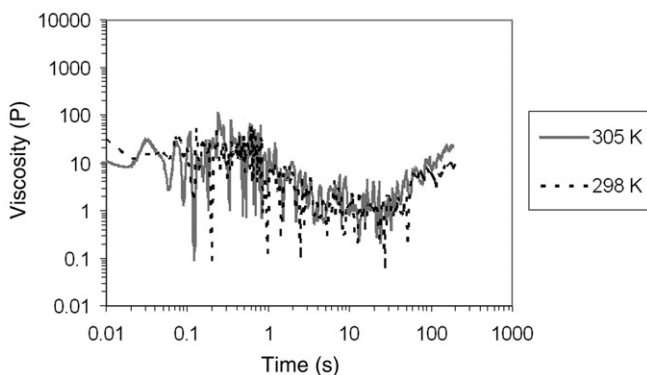


Figure 8. Transient viscosities for *n*-heptadecane C17, at 298 and 305 K, both curves were executed at the fixed shear rate of 10^{-2} s^{-1} .

Note: The time interval between a measure and following one is 0.01 s.

rheological properties. At low shear rate and in the shear thinning region, the viscosities of pure C20, as well as those of the mixture with molar fraction of 0.82, increased with increasing test temperatures. There are two blocks: one in the range 315–325 K, and another for the range 345–355 K (Figure 3). What is usually expected is a behaviour more similar to that of C17, where the viscosities decrease with a temperature increment (Figure 2). Nevertheless, even for C17, this behaviour is not clearly marked.

This behaviour, which is reproducible, can be attributed to a residual structure formation of the solid phase in alkanes, similar to that of liquid crystals. On one hand, for low temperatures (close to the melting point), a reasonable behaviour would be in favour of easy self-organisation (orientation) of the chains along the flow direction. On the other hand, high temperatures promote a higher degree of disorder, but alkane chains can sustain more complex conformations with increasing viscosity as well.

By increasing the test temperature, and after the shear thinning region, the viscosities tend to coincide. A slight shear thickening behaviour has also been observed for increasing temperature.

Several published works report the anomalous behaviour for the linear alkanes' heat capacity, just above the melting point [13]. That is, there is an excess enthalpy that disappears within a span of about 30 K above the melting point. This excess enthalpy may correspond to an increase in entropy for a fully randomised liquid, destroying the ordering of a liquid crystalline state [13]. This effect is still present in the mixture with abundance of C20 (Figure 5). Although, in this case the 'temperature thickening' is not regular, e.g. at 383 K the viscosity curve is lower than that of 355 K, because increasing the temperature too much means overcoming the temperature range in which the alkanes can exhibit ordering in the liquid phase. On the other hand, the mixture poor in C20 (Figure 6) reflects more the properties of C17, for which this behaviour cannot be detected.

The proposed interpretation can be supported by the direct estimation of the entropy of pure eicosane due to shear steady flow. On this regard, non-equilibrium

thermodynamics can give another insight into this phenomenon [14]. Entropy production per unit volume and unit time σ is given by the following equation:

$$\sigma = -\frac{\bar{J}_q \bullet \bar{\nabla} T}{T} + \frac{1}{T} \bar{\bar{\tau}} : \bar{D} = \sigma_Q + \sigma_W, \quad (1)$$

where \bar{J}_q is the heat flow, T the absolute temperature, $\bar{\bar{\tau}}$ the viscous stress tensor, \bar{D} the rate of strain tensor, σ_Q the entropy production due to heat flow and σ_W that due to shear work. The entropy production due to shear flow can be easily calculated through the following equation [14]:

$$\sigma_{W,T} = \dot{\gamma} \frac{\tau}{T} = \frac{\eta(\dot{\gamma})\dot{\gamma}^2}{T}, \quad (2)$$

where $\dot{\gamma}$ is the shear rate, $\eta(\dot{\gamma})$ the viscosity dependent on the shear rate for non-Newtonian flow and τ the shear stress. The production of entropy can be expressed as the product of a flux by the corresponding entropy derivative [15]

$$\sigma = \sum_i \dot{\alpha}_i \left(\frac{\partial s}{\partial \alpha_i} \right)_X = \sum_i \sigma_i, \quad (3.1)$$

and the derivative can be so expressed

$$\left(\frac{\partial s}{\partial \alpha_i} \right)_X = \frac{\sigma_i}{\dot{\alpha}_i}, \quad (3.2)$$

where $\dot{\alpha}_i$ is the flux associated to the variable α_i , and X the constant variable at which the derivative is calculated. According to Equation (3.2), as the viscosity measured is a steady-state value at a fixed shear rate, it is possible to define an entropy derivative with respect to the shear deformation γ in the following way, taking as flux the shear rate $\dot{\gamma}$

$$s'_T = \left(\frac{\partial s}{\partial \gamma} \right)_T = \frac{\sigma_{W,T}}{\dot{\gamma}}. \quad (4)$$

At low shear rates, the entropy derivative s'_T of eicosane at 345 K, calculated through Equation (4), has the highest values, and that at 315 K has the lowest ones, as shown in Figure 9. All the values of s'_T increase slightly at low shear rates, between 10^{-4} and 10^2 s^{-1} , but tend to increase awfully and be similar at high shear rates in spite of the different temperatures.

Moreover, the entropy derivative s'_T can be given by the following expression, if the specific heat in the considered range of temperatures does not depend on temperature in a marked manner, as expected in the presence of an excess specific heat [13]

$$s'_T = \left(\frac{\partial s}{\partial \gamma} \right)_T = \frac{\partial}{\partial \gamma} \left(\int_{T_f}^T \frac{c_p}{T} dT + c \right) \approx \left(\frac{\partial c_p}{\partial \gamma} \right)_T \ln \frac{T}{T_f}; \quad (5)$$

where c_p is the specific heat and T_f the melting temperature of the considered alkane. The ratio between s'_T and the logarithm of Equation (5) leads to a new set of curves of normalised entropy. All the curves are now close and with very low values, near to $0 \text{ J K}^{-1} \text{ m}^{-3}$, at low shear rates (Figure 10), and only very far from equilibrium at

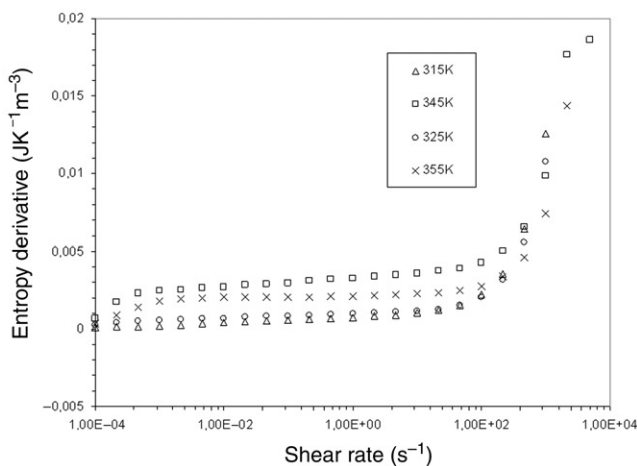


Figure 9. Entropy derivative s'_T for *n*-eicosane C20 at different temperatures.

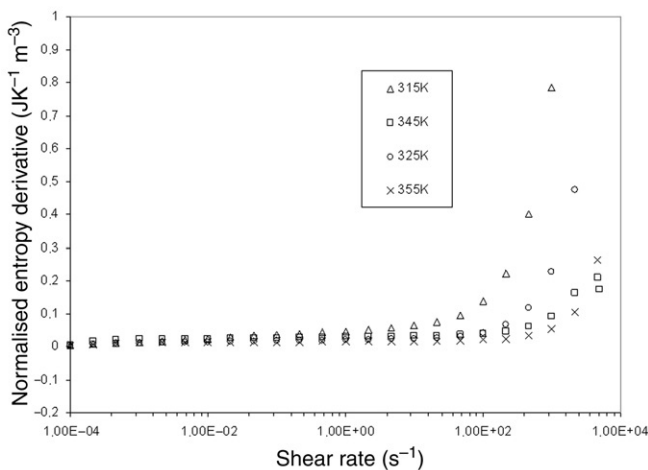


Figure 10. Normalised entropy derivative for *n*-eicosane C20 at different temperatures.

high shear rates they are split. This indicates a strong dependence of s'_T on temperature at low shear rates rather than on the derivative of specific heat, which should have very low and constant values according to the results shown in Figure 10.

Therefore, this apparent anomalous behaviour at low shear rates, i.e. near equilibrium, seems to be linked to the accumulated entropy, which hardly affects viscosity, and consequently the entropy production.

The curves of the first coefficient of normal stresses Ψ_1 for eicosane, at different temperatures, are very similar (Figure 4(a)). Although, these curves are closer than the viscosity curves (Figure 3) and there is no clear temperature dependence.

In addition, the quotient ψ_1/η has been taken into account, which shows the relation between the elastic (reversible) part of the flow process and the dissipative

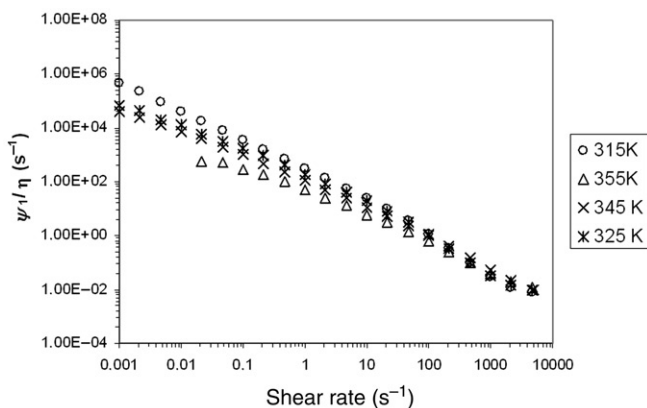


Figure 11. Quotient ψ_1/η for eicosane at different temperatures.

(irreversible) part, related to the production of entropy. The curves of this quotient for pure eicosane (Figure 11) show that dissipative processes prevail at high temperatures and low shear rates, while at high shear rates all the curves tend to overlap.

All these results together confirm that the cumulated entropy is the main cause of the behaviour of ‘temperature thickening’, and specifically the logarithm of Equation (5) acts as scale factor for eicosane entropy at low shear rates. This is in favour of the above reported interpretation of a certain degree of order at temperatures close to the melting point, which is subsequently disrupted either by temperature or by high shear strains.

The transient test for C20 was carried out at 315 K, and at the shear rate of 10^{-2} s^{-1} , i.e. at about 4 K more than melting point temperature. The transient tests for C17 were carried out at the shear rate of 10^{-2} s^{-1} , at 298 and 305 K, i.e. about 4 and 11 K more than the melting point, respectively. The viscosity of C20 reaches the steady state quicker and with fewer oscillations (Figure 7) than C17 (Figure 8). These oscillations may represent the characteristic initial rotations of entangled chain polymers induced by shear stresses, before these align preferentially along the flow directions. The minor extent of this phenomenon for C20 sample indicates that, in this case, the degree of order in the flow direction is reached readily, probably due to the existence of domains with a certain degree of order before flow field actually begins.

5. Conclusions

The viscosity of eicosane and that of mixtures with a high content of eicosane exhibit a ‘temperature thickening’ behaviour at low shear rates. This phenomenon can be attributed to an entropic effect, as shown by the curves of the normalised derivative of entropy with respect to shear deformation for eicosane, which are all overlapped at low shear rates. This indicates that the logarithm of the ratio between the test temperature and the melting temperature acts as scale factor, in this specific case at

low shear rates, and that the ‘temperature thickening’ behaviour may be due to the cumulated entropy, which hardly affects viscosity, and consequently the entropy production. In favour of this interpretation, also the curves of the quotient ψ_1/η show that for high temperatures dissipative (irreversible) processes prevail on elastic (reversible) ones. This behaviour is not clearly identified in heptadecane, and in mixtures with few eicosane is not detected.

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