

Influence of salinity on the slip velocity of xanthan gum solutions

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The influence of three different salts (KCl, 0.0002 M; CaCl₂, 0.0001 M; NaCl, 0.0002 M) on the slip velocity of 0.3% xanthan solutions, around the corresponding order-disorder conformational transition temperature, was investigated with a glass capillary rheometer. An enhancement of the slip velocity was observed very near the transition for the three salts studied. This result is similar to the one reported by us, using two different xanthan samples in the absence of salt. The behavior of the power-law parameters of the slip velocity was similar to the one obtained with xanthan without salt around the transition temperature. Slip was determined with the Mooney method, showing good results and only small discrepancies at higher temperatures ($T > 34^\circ\text{C}$).

Keywords: Capillary rheometer; slip velocity; xanthan solutions; transition temperature

En este trabajo se investiga la influencia de tres sales diferentes (KCl, 0.0002 M; CaCl₂, 0.0001 M; NaCl, 0.0002 M) sobre la velocidad de deslizamiento de soluciones acuosas de xantana al 0.3% en el intervalo de temperatura donde ocurre la transición conformacional orden-desorden de la xantana. Las mediciones de velocidad de deslizamiento fueron realizadas con un reómetro de capilar de vidrio con una razón longitud/diámetro de 640. Un aumento en la velocidad de deslizamiento fue encontrado cerca de la temperatura de transición para las tres sales utilizadas, similar al comportamiento encontrado en ausencia de sales. El deslizamiento fue determinado usando el método de Mooney y el método de Piau y colaboradores mostrando una proporcionalidad independiente del diámetro de los capilares y el tipo de sal utilizado y un valor casi constante en todo el intervalo de temperaturas utilizado (26–39°C).

Descriptores: Reómetro de capilar; velocidad de deslizamiento; soluciones acuosas de xantana; temperatura de transición

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1. Introduction

Most studies dealing with xanthan gum solution rheology have been conducted at salt and temperature conditions such that the molecule is stabilized in the ordered rigid-rod conformation [1–4]. In common with charged polions the thermal stability of xanthan conformation is largely affected by the ionic environment. Besides this, several other factors are known to influence the thermal properties of xanthan, such as the degree of acetyl and pyruvate substitution [5]. Such temperature dependence begins to diminish at concentrations below 1 mg/ml [2].

The two extreme conformational states in which the xanthan molecule is known to exist, namely the ordered helical rodlike or as a fully disordered coil, have been investigated and probed by a number of physical techniques [6–8]. The mid-point order-disorder conformational transition temperature (T_m) can be shifted in temperature by modifying the type and concentration of salt [6, 9].

The slip phenomenon of xanthan solutions has been studied extensively in the last years [10, 11]. It is originated by a strong alignment of molecules near the walls with the flow and migration through regions of lower shear stress, originating a low concentration layer adjacent to the walls [12, 13]. The slip velocity has been traditionally measured by the method developed by Mooney in 1931 [14]. After Mooney other authors have proposed alternative methods to measure slip in capillaries [15, 16]. We have shown in a previous paper that only the Mooney method and the method developed by Piau *et al.* are adequate to measure slip of xanthan solutions [17].

It is well known that the slip phenomenon depends on the structure and conformation of the molecules. De Vargas *et al.* [18] have demonstrated experimentally that flexible macromolecules of polyethylene oxide (PEO) and polyacrylamide do not show slip in glass capillaries at relative small stress; the same results were found in our laboratory. An excellent review on the subject has been recently published by

Agarwal *et al.* [19], where the slip phenomenon is extensively discussed.

On a recent account, we have recently demonstrated [17], that the experimental slip velocity measurements of two different xanthan gum solutions, show an abrupt change around the T_m of the xanthan molecule. The aim of the present study was to show that the change in slip velocity is more pronounced around the xanthan T_m , and that this effect is consistent with the shift in xanthan T_m in the presence of different type of salts (NaCl, KCl or CaCl₂).

In the next section we explain the experimental details, in Sect. 3 basic theoretical concepts are explained, results are given in Sect. 4 and finally in Sect. 5 some conclusions are discussed.

2. Experimental

The experiments were performed in a capillary rheometer designed and constructed in our laboratory and described elsewhere [17]. It was calibrated with a newtonian solution of 70% glycerol (J.T. Baker, density 1.2576 g/cm³ and molecular weight 92.10) in deionized water at 20°C. We performed viscosity measurements with three different capillaries of a 0.6% polyacrylamide aqueous solution and compared with the results of a Brookfield cone and plate viscometer. The observed differences in the flow curves were less than 2%.

The pressure drop was determined by using a Validyne pressure transducer. Using a hydrostatic head, the pressure was varied and the uncertainty in the pressure measurements was kept constant to within 2%. The volumetric flow rate was determined by using an analytical balance and a stop watch and the uncertainty in the volumetric flow was kept less than 0.1%. The shear rate and shear stress obtained in the experiments were in the range of 50–600 s⁻¹ and 3–7 Pa, respectively.

The experiments were carried out at constant temperature using a circulating water bath controlled to within ±0.2°C. Allowance for evaporation losses at the outlet of the capillaries was made using distilled water as a reference.

Samples of xanthan gum (Gum Xanthan, Aldrich Chem Co., Cat. No. 28602-8 lot no. 05119MG) solutions were prepared using deionized water as described previously [17]. They were run through a capillary of known flow curve, the accepted differences in the flow curves for different solutions were less than 2% in $\dot{\gamma}$.

The mid-point order-disorder transition temperature T_m region of xanthan solutions was determined by measuring intrinsic viscosity at different temperatures in the range 24 to 36°C.

The intrinsic viscosity of aqueous xanthan solutions was measured with a modified Ubbelohde viscometer (cat. 7987-05 size 0.6 mm.), immersed in a water bath circulating at different temperatures.

The experiments were performed for $L/D = 640$, the diameters used were 0.228, 0.126 and 0.090 cm. All diame-

ters were determined by using mercury with a precision of ±0.2%.

Three different salts (NaCl, 0.0002 M; KCl, 0.0002 M and CaCl₂, 0.0001M) were used in order to shift xanthan T_m .

In order to maintain a constant ionic environment in the solutions, electrical conductivity was measured on a HORIBA ES-14E conductimeter. A Brookfield model LVDV-III viscometer fitted with a cone (CP 51 cone angle 1.565°) was used to measure steady shear viscosity.

3. Theory

The pressure drop between the capillary ends and the volumetric flow (Q) were measured for the xanthan solutions and from these data the apparent wall shear rate ($\dot{\gamma}_w$) and the wall shear stress (τ_w) were determined neglecting end effects. End effects can be neglected for capillaries with $L/D \geq 500$ as was demonstrated by De Vargas *et al.* [10]. Under such conditions, a fully developed flow is achieved and the flow curves become practically independent on the end effects.

The wall shear stress τ_w can be obtained experimentally by use of the relationship:

$$\tau_w = \frac{P_1 - P_2}{4(L/D)}, \quad (1)$$

where P_1 and P_2 are respectively the measured pressures at the entry and exit of the capillary. From the Poiseuille theory the apparent wall shear rate $\dot{\gamma}_w$ is given by

$$\dot{\gamma}_w \equiv \frac{32Q}{\pi D^3}. \quad (2)$$

According to the Mooney theory [14], the slip phenomenon is interpreted as an abnormally large velocity gradient in a very thin layer adjacent to the capillary walls. The slip was considered mathematically as a discontinuity in the velocity of the fluid. The thickness of the layer was considered very small in comparison with the capillary radius. The slip velocity v_s is defined as

$$v_s = \tau_w \beta, \quad (3)$$

where β is a constant slip coefficient and τ_w is the wall shear stress given by Eq. (1).

After several steps and using a change in the variable of integration, Mooney obtained the relationship:

$$\frac{32Q}{\pi D^3} = 8 \frac{v_s}{D} + \frac{4}{\tau_w^3} \int_0^{\tau_w} \dot{\gamma} \tau^2 d\tau, \quad (4)$$

where $\dot{\gamma}$ and τ are respectively the shear rate and the stress at a distance r from the wall and Q is the measured flow rate.

Therefore, for a given value of the wall shear stress, a plot of $\dot{\gamma}_w$ as a function of the reciprocal of the diameter $1/D$, will produce a straight line of constant slope of magnitude $8v_s$.

Equation (4) can be expressed by the relationship

$$\dot{\gamma}_w = \dot{\gamma}_\infty + \frac{8v_s}{D}, \tag{5}$$

where $\dot{\gamma}_\infty$ denotes the apparent wall shear rate extrapolated to infinite diameter in absence of slip.

This method to calculate the slip velocity does not consider end effects and a unique curve is obtained for different diameter of the capillaries for each set of L/D 's.

Piau *et al.* [15] have developed a method to measure wall slip in capillaries considering the entrance head losses of the capillaries for a fluid based on a power law. This equation is

given by the expression

$$\begin{aligned} \dot{\gamma}_w &= \frac{3n+1}{n} \frac{Q}{\pi R^3} \\ &= \frac{3n+1}{n} \frac{v_s}{R} + \left[\frac{R}{2kL} (\Delta P_t - \Delta P_e) \right]^{1/n}, \end{aligned} \tag{6}$$

where n and k are the power - low parameters, R the capillary radius, ΔP_t and ΔP_e the total and entrance head losses of the capillary, respectively, and the other parameters were defined above.

As a final result, the relationship giving the wall slip velocity is given in Eq. (5) in the appendix of the work of Piau *et al.* by the expression

$$\frac{3n+1}{n} v_s = \left[1 + \frac{p}{n} \left(\frac{\tau_w - \frac{R}{2L} \Delta P_e}{k} \right)^{-1 + (1/n)} \frac{R \Delta P_e}{2L k \dot{\gamma}_w} \right] \left[\frac{d\dot{\gamma}_w}{d(1/R)} \right]_{\tau_w} - \frac{R^2 \Delta P_e}{2L kn} \left(\frac{\tau_w - \frac{R}{2L} \Delta P_e}{k} \right)^{-1 + (1/n)} \tag{7}$$

When L/R approaches infinity or the entrance head losses ΔP_e are very small we obtain the slip velocity

$$v_s = \frac{n}{3n+1} \left[\frac{d\dot{\gamma}_w}{d(1/R)} \right]_{\tau_w}. \tag{8}$$

Hatzikiriakos and Dealy [16] have introduced a new method to measure slip in capillaries for molten polyethylenes using only one flow curve. In this way, the slip velocity could be determined from the basic capillary flow data and this velocity can be calculated from a single apparent flow curve (τ_w vs. $\dot{\gamma}_w$) while the Mooney and Piau methods requires at least three flow curves with the same L/D ratio and different diameters. Results obtained in a previous paper [17] show that the method developed in Ref. 16 is not appropriate to determine slip on semidilute xanthan solutions. On the contrary the slip velocity obtained with the Mooney method and the one derived with the method developed by Piau *et al.* resulted proportional.

4. Results

The curves τ_w vs. $\dot{\gamma}_w$ show the typical power-law relationship ($K\dot{\gamma}_w^n$) with an average correlation R around 0.99 for all the curves. However, higher correlations were found ($R \geq 0.999$) by adjusting a second order polynomial relationship.

The parameter n (average 0.33) did not depend appreciably on the type of salt and the capillary diameter and a slight dependence on the temperature was observed, showing a lower value (approximately 0.32) at 28°C and 0.35 at 38°C.

The slip velocity was determined by measuring the quantity $[d\dot{\gamma}_w/d(1/D)]_{\tau_w}$ using three different capillary diameters by fitting straight lines with Eq. (5).

In the limit of large capillary diameters, we found that the difference of the slip velocity determined with the Mooney method and the one determined with the method of Piau *et al.* was practically independent of the type of salt used and independent of temperature. According to Eq. (8), the factor $4n/3n+1$ gives an average value of 0.66.

Figure 1 shows the corresponding flow curves $\dot{\gamma}_w$ vs. τ_w for several temperatures, using the cone and plate viscometer, and $\dot{\gamma}_\infty$ vs. τ_w using the apparent wall shear rate extrapolated to infinite diameter in absence of slip obtained from Eq. (5). The average differences between readings on both flow curves were within 2% demonstrating the applicability of the Mooney method.

Holzwarth [9] has shown that the transition temperature of xanthan samples increases with increasing salt concentration for both Na^+ and Ca^{+2} and has observed that Ca^{+2} is effective at lower concentrations than Na^+ . We observed the same behavior using salt concentrations of 0.0002 M for NaCl and KCl and 0.0001 M for CaCl_2 .

Figure 2 shows the slip velocity of a 0.3% xanthan solutions with the concentrations of the three salts mentioned above. The results are similar to the ones found before without added salts [17].

An enhancement of the slip phenomenon is produced for the different salts around the transition temperature, demonstrating the high sensibility of the capillary rheometer to detect the transition temperature of xanthan samples. The measured transition temperature of our xanthan samples was approximately 29–30°C for the concentrations of the salts used.

Figure 3 shows the Mooney plots for the three different salts used at 30 °C and for the three different diameters. The relationship between the shear rate and the inverse of the di-

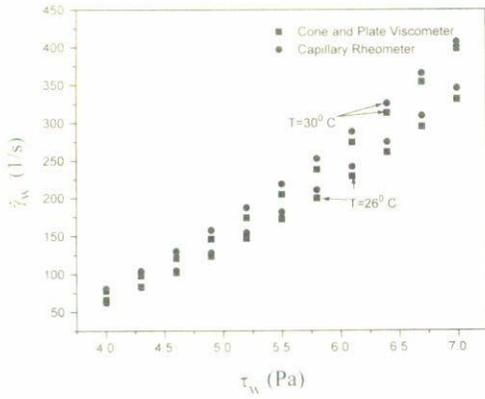


FIGURE 1. Flow curves of 0.3% xanthan solution in 0.0002 M NaCl at two different temperatures comparing the measured shear rate with a cone and plate viscometer and the extrapolated shear rate $\dot{\gamma}_w$ to infinite diameter obtained from the capillary rheometer.

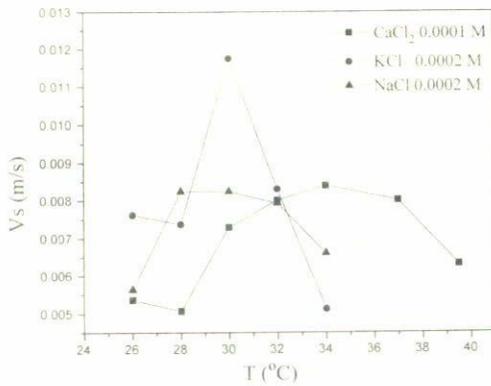


FIGURE 2. Slip velocity measurements around the transition temperature of 0.3% xanthan solutions, using three different salts: CaCl_2 , 1×10^{-4} M; NaCl, 2×10^{-4} M and KCl, 1×10^{-4} M. The wall shear stress was kept constant (5.5 Pa).

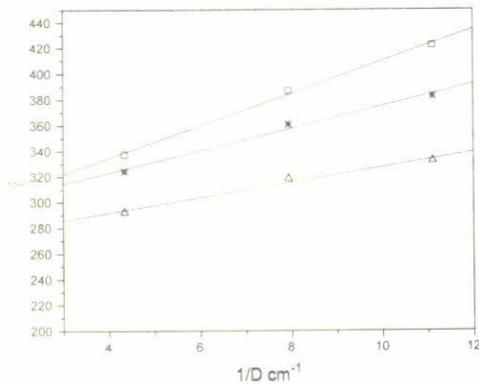
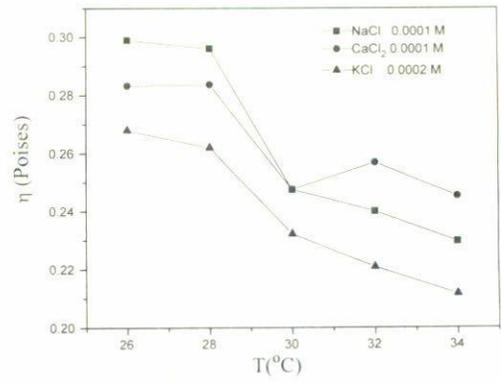
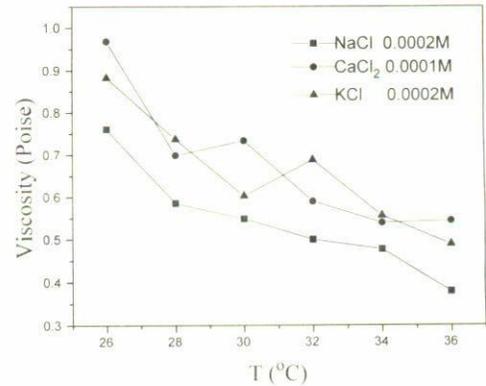


FIGURE 3. Mooney plots for 0.3% xanthan solutions at 30°C for the three salts used and for the wall shear stress 6.1 Pa. 2×10^{-4} M NaCl; 2×10^{-4} M KCl and 1×10^{-4} M CaCl_2 .

ometer is a straight line with a very good correlation (≥ 0.99) and the slope of the curves gives the slip velocity according with Eq. (5).



(a)



(b)

Figure 4. (a) Apparent viscosity, using the capillary rheometer, around the transition temperature of 0.3% xanthan solutions with the same salt concentrations as in Fig. 2. The capillary diameter used was 0.09 cm, and the wall shear stress was kept constant (5.5 Pa). (b) Shear viscosity, measured with a cone and plate viscometer, around the transition temperature of 0.3% xanthan solutions with the same added salts as in Fig. 4a, and the shear stress 5.5 Pa.

Dividing Eq. (1) by Eq. (2) we obtain the apparent viscosity (η) for each diameter of the capillar used. As is shown in Fig. 4a, η changes more abruptly around the transition temperature when it is measured with the capillary rheometer. The average viscosity changes for the three salts between 28 and 30°C are about 0.04 poise. On the contrary, such variations can not be easily detected by using a cone and plate viscometer, obtaining smaller changes of the curvature around the transition temperature as can be seen in Fig. 4b. This could probably be due to the influence of the geometry on the viscosity measurements.

The slip velocity in Fig. 5 shows the known power law behavior ($K \tau_w^n$) for the three different salts. The slip velocity results are dependent on the type of salt, showing larger values for KCl around the transition temperature. The behavior of the power-law parameters is similar to the one reported before, where K finds a relative maximum and n a relative minimum near the transition temperature. The power law parameters are given in Table I for the different salts used.

TABLE I. Power-law parameter of the slip velocity ($V_s = K\tau_w^n$) for 0.3% xanthan solutions with the three salt concentrations used. V_s is given in m/s and τ_w in Pa.

T ($^{\circ}\text{C}$)	KCl		CaCl_2		NaCl	
	n	K	n	K	n	K
26	3.012	4.9×10^{-5}	3.30	1.8×10^{-5}	2.81	6.0×10^{-5}
28	2.633	8.6×10^{-5}	3.26	2.0×10^{-5}	2.57	1.1×10^{-4}
30	2.896	7.8×10^{-5}	3.974	4.2×10^{-5}	2.81	6.0×10^{-5}
32	3.012	4.9×10^{-5}	3.22	3.2×10^{-5}	2.85	6.2×10^{-5}
34	3.695	9.9×10^{-6}	3.869	7.4×10^{-6}	3.42	1.9×10^{-5}

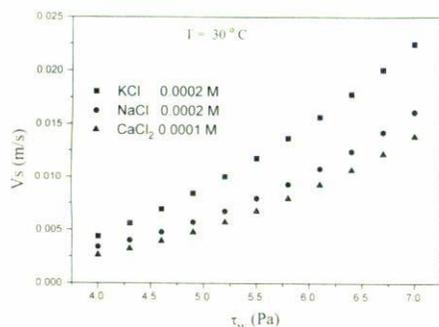


FIGURE 5. Slip velocity vs. wall shear stress behavior of the same samples. The temperature (30°C) corresponds to the maximum of slip velocity obtained when used KCl.

5. Conclusions

In this work we have investigated the influence of three different salts (NaCl, KCl and CaCl_2) on the slip velocity of 0.3% xanthan solutions around the transition temperature. This order-disorder transition temperature was shifted due to the salinity effects and an enhancement of the slip velocity around this temperature was obtained for the three cases.

The Mooney method, used to obtain the slip velocity, resulted appropriate to measure the slip phenomenon and only

small deviations were detected at relative higher temperatures ($T > 34^{\circ}\text{C}$). The apparent viscosity measured with capillary rheometer showed more sensibility around the transition than that obtained with a cone and plate viscometer due to the influence of walls. The power-law parameters obtained for the slip velocity showed the same qualitative behavior as the one reported before for two different samples of xanthan gum in the absence of salt.

In spite of the difficulties to measure slip by using the Mooney method, the capillary rheometer has shown to be a sensible and useful tool to determine the behavior of the slip velocity around of the order-disorder transition temperature of xanthan gum and this could be used to complete the characterization of the transition and understand the relationship between molecular conformation and the rheological properties of xanthan solutions and other macromolecules.

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