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Viscosimetric behaviour of carboxymethyl cellulose – Arabic gum mixtures: A new step to modelling

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ABSTRACT

The rheological properties of carboxymethyl cellulose and Arabic gum mixtures under different experimental conditions have been studied. It has been determined the influence of the shear rate on different polymers ratios in aqueous solutions upon the apparent viscosity. The important effect caused by temperature on the rheological behaviour of polymer mixtures aqueous solutions has also been studied. Characteristic behaviours have been found with clear deviations from the linear trends that involve the existence of interactions between polymers. A model based on an additive rule has been improved to generalize the use at different experimental conditions employed in the present work.

1. Introduction

One of the most important transport properties in processes that involve polymers is the viscosity of their solutions (Sovilj & Petrovi, 2007). An accurate quantitative model equation to determine the viscosity is essential for the detailed design and modelling of the equipment, such as piping, pumps and heat exchangers. The viscosity of mixtures that contain polymers is much more difficult to predict than the viscosity of mixtures with low molecular weight components because polymers commonly show a complex rheological behaviour.

In the present work, aqueous solutions of gums have been used. Gums are high molecular weight hydrophilic biopolymers, and they are widely used in food industry to control functional properties of food products. The most important properties of a solution made from gum, in terms of gelling and shear-thinning, are water binding and viscosity. In addition to these functions, they are also used in food formulations for emulsion stabilization, prevention of ice recrystallization and sensory attributes. There are many types of hydrocolloids available in the market, from plants, seaweeds, microbial or synthetic origin. They are also obtained by chemical or enzymatic treatment of starch or cellulose (Dickinson, 2003).

The resulting rheological properties of these solutions vary, in general, depending on the polymer concentration, molecular weight, temperature and shear rate. The rheological properties of gums are particularly important when used in the formulation of any food, due to its effect on the texture attributes.

The use of two or more polymers in the formulation of a food is put into practice in the industry to achieve a synergistic effect (Ahmed, Ramaswamy, & Ngadi, 2005). The product quality could be improved by means of a synergism of polymer properties. Polymers can attribute better rheological properties to the product, which may also bring about a cost reduction during manufacture (Williams & Phillips, 2000). Synergetic effects have been found by different researchers (Álvarez-Lorenzo et al., 2001; Khouryieh, Herald, Aramouni, & Alavi, 2006; Song, Mathias, Tremblay, & Chen, 2003) in aqueous solutions of different polymer blends. The influence of the mixture upon the viscosity has different behaviours in function of the polymers employed, obtaining (i) positive deviation blends, (ii) negative deviation blends and (iii) positive and negative deviation blends. Positive deviation behaviour is normally associated with blends exhibiting strong interactions between the phases, and negative deviations are attributed to the occurrence of slip, caused by a lack of adhesion (weak interactions) between the two polymers.

In example, the mixture of carboxymethyl cellulose and hydroxyethylcellulose in homogeneous media exhibit viscosity synergism with positive deviations and also with a clear influence of shear rate upon the magnitude of the deviation (Zang, 1999). On the other hand, the negative deviation type has been found more frequently in different systems: synthetic and natural polymers (Chu, Chiu, & Tseng, 1994; Gómez-Díaz, Navaza, & Quintáns-Riveiro, 2008b; Mikkonen & Savolainen, 1990).

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The influence of composition on rheological behaviour in synthetic polymer mixtures (Song et al., 2003) has also been studied in previous works, and clear negative deviations as regards the linear behaviour (ideal behaviour) were found. These researchers have developed an additive rule modification based on a well-known equation to fit the behaviour shown by the polymers mixtures. The use of this equation implies the knowledge of the Newtonian viscosity (at high shear rate values) that involves the use of different equations.

The system employed in the present work is based on the mixture of aqueous solutions of two hydrocolloids (carboxymethyl cellulose and Arabic gum) and the studies included in this manuscript involve the rheological behaviour. The rheological behaviour of aqueous solutions of each polymer employed in present work have been previously analysed (Gómez-Díaz & Navaza, 2003; Gómez-Díaz, Navaza, & Quintáns-Riveiro, 2008a) showed a pseudoplastic behaviour. Also, these previous studies reached the conclusion that Ostwald model fits the influence of shear rate upon apparent viscosity satisfactorily.

Present work includes a modification in an additive rule to fit the experimental results using a more general equation, that could be used under all the different experimental conditions has been developed in present work and it improves the correlation to fit this kind of complex behaviour.

2. Materials and methods

Carboxymethyl cellulose and Arabic gum polymers were supplied by Aldrich and Fluka, respectively. The solutions were prepared by mass using a balance with a precision of 10^{-7} kg. Distilled water was used to prepare the polymers solutions. The carboxymethyl cellulose (CMC) and Arabic gum (AG) aqueous solutions characterization and rheology have been published previously (Gómez-Díaz & Navaza, 2003; Gómez-Díaz et al., 2008a). In the present study, aqueous solutions of Arabic gum and carboxymethyl cellulose were mixed to provide samples with high, medium and low concentrations of both polymers.

Five mixtures have been analysed in present work: mixture A (100 g L^{-1} AG + 2 g L^{-1} CMC), mixture B (300 g L^{-1} AG + 4 g L^{-1} CMC), mixture C (400 g L^{-1} AG + 8 g L^{-1} CMC), mixture D (400 g L^{-1} AG + 2 g L^{-1} CMC) and mixture E (100 g L^{-1} AG + 8 g L^{-1} CMC). These solutions were blended at the following ratios: 100% CMC:0% AG, 80% CMC:20% AG, 60% CMC:40% AG, 40% CMC:60% AG, 20% CMC:80% AG and 0% CMC:100% AG. Freshly prepared CMC and AG solutions were mixed at room temperature and were stirred until complete mixing. Different amounts of NaCl were added to solutions to analyse the effect of this electrolyte upon de rheological behaviour and to obtain information about polymers interaction.

An Anton Paar DV-1P digital thermostated rotational viscometer with two coaxial cylinders was used to carry out the rheological measurements. This equipment allows the variation of shear rate in a wide range by the use of different spindles.

The effect of temperature upon the rheological behaviour was also analysed. To carry out this study, the rotational viscometer was connected to a thermostat-cryostat (Selecta Frigitherm) and aqueous solutions of polymers were thermostated at temperatures from 10 to 50 °C. For each temperature, the effect of shear rate and mixture composition was analysed.

The experiments were conducted in triplicates and mean and standard deviation were calculated. The error bars in the graphs are the standard deviation (calculated by means of Eq. (1)) of means from three replications. Curve fitting was performed using the Grafit v.5.0 software package. Fit parameters were determined by linearised by taking the logarithmic terms.

$$\sigma = \left(\frac{(\eta_{\mathrm{cal}} - \eta_{\mathrm{exp}})^2}{n-1} \right)^{1/2} \qquad (1)$$

where η is the viscosity value and n is the data number.

3. Results and discussion

The rheological behaviour of systems formed by aqueous mixtures of carboxymethyl cellulose and Arabic gum has been determined analysing the shear rate influence on the apparent viscosity. An example of the experimental data is shown in Fig. 1 for the mixture A and a composition relation of CMC:AG = 80%/20% and under two different temperatures. The experimental data included in Fig. 1 show that there is an influence of both variables (shear rate and temperature) upon the apparent viscosity. An increase in both variables produces a decrease in the apparent viscosity value and the trend observed for the shear rate influence is potential. In relation to the shear rate effect, this behaviour is higher at the low shear rate values in the studied range because when this variable increases in the employed range, the influence of the shear rate decreases until a viscosity constant value.

The behaviour observed in Fig. 1, previously commented, indicates that the shear rate and temperature have an influence upon the rheological behaviour of aqueous solutions of polymers mixtures. The influence caused by the temperature seems more important than the effect caused by shear rate. This kind of influence depends on the mixtures composition but the effect of these two variables has the same global effect, producing a decrease in the value of apparent viscosity when the shear rate and temperature increase. The influence of temperature upon the apparent viscosity is common but, in the case of shear rate, the obtained behaviour indicates that these kinds of polymer mixtures show a pseudoplastic behaviour.

This rheological behaviour has been observed for all the samples analysed in the present work, and it is in agreement with the previous results determined for the aqueous solutions of carboxymethyl cellulose (Gómez-Díaz & Navaza, 2003) and Arabic gum (Gómez-Díaz et al., 2008a) employed to formulate the mixtures used in this work. The rheological characteristics of these systems (non-Newtonian and pseudoplastic) imply the reduction in the apparent viscosity when the shear rate applied to the liquid phase increases.

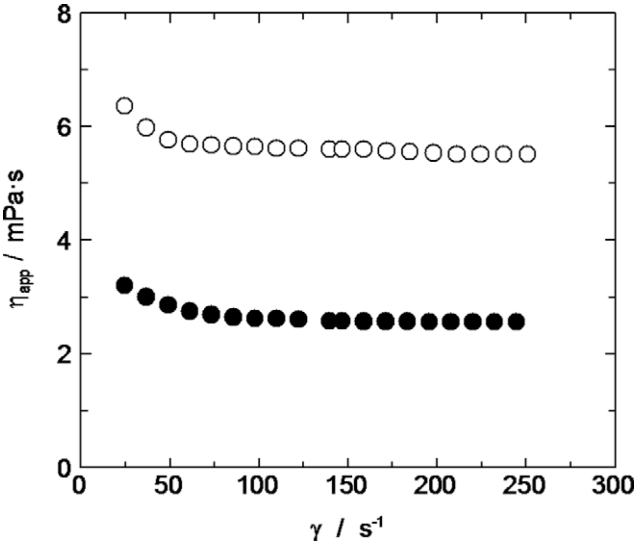

Fig. 1. Influence of shear rate upon apparent viscosity. Mixture A. CMC:AG ratio = 80%/20%. (○) t = 10 °C; (●) t = 30 °C.

Plotting the experimental results about the influence of the shear rate upon the shear stress allows us to confirm the previously commented rheological behaviour shown in Fig. 1. Different models have been employed in literature to fit the experimental data such as Ostwald, Sisko, Carreau model, etc. However, for this kind of systems, the use of Ostwald model is suitable for its simplicity and good agreement with the experimental apparent viscosity and shear stress data (Gómez-Díaz & Navaza, 2003; Gómez-Díaz et al. 2008a).

An important part of the present study based on rheology of aqueous systems based on the mixture of two polymers, is the influence of mixture ratio and composition of the solutions blend upon the rheological behaviour and apparent viscosity. Figs. 2 and 3 show examples of the experimental data obtained for the influence of composition upon the viscosity of these systems and also include the influence of shear rate and temperature. Specifically, Fig. 2 shows the influence of mixtures composition and shear rate upon viscosity and the experimental results indicate that the shear rate produces a decrease in the value of this physical property previously commented, but this effect is not very pronounced. In relation with the influence of mixtures composition upon viscosity, Fig. 2 shows a decrease when CMC presence increases due to the CMC aqueous solution viscosity employed in mixture B is minor than the corresponding one for AG. Another interesting variable analysed in present work has been the temperature, and Fig. 3 shows the combined influence of composition and temperature upon the viscosity value and a clear decrease in the value of this property was found and more important effect is observed when temperature is varied in the low employed range.

On the basis of the experimental results we conclude that the influence caused by shear rate and temperature produces in all cases a decrease in the value of apparent viscosity, with similar trends than experimental results obtained for other researchers for similar systems (Cancela, Álvarez, & Maceiras, 2005). Then the mixture of aqueous solutions of CMC and AG produces samples with similar rheological properties in relation with shear rate influence. The results obtained for the experimental systems formed by both polymers in relation with the influence of shear rate and temperature upon viscosity are in agreement with the previous studies performed for aqueous solution of each polymer (Gómez-Díaz & Navaza, 2003; Gómez-Díaz et al., 2008a).

If we concentrate studying the influence of mixture compositions, a complex behaviour has been obtained, observing that this trend indicates there is a separation from the linear behaviour between the viscosity value for the individual mixtures. Fig. 4 show other example of the experimental results obtained in the present work to analyse the influence of a mixture composition. The deviations observed as regards the ideal behaviour or linearity have been observed for all the mixtures analysed in the present work. The experimental viscosity takes values minor than the corresponding ones predicted by ideal models, so negative deviations were obtained for all the experimental systems. This behaviour is in agreement with previous studies for other systems formed by polymer mixtures (Song et al., 2003; Gómez-Díaz et al., 2008a, 2008b).

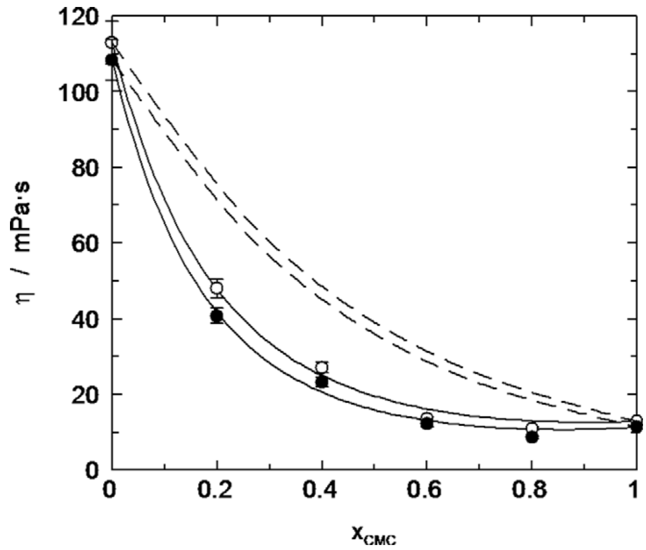

Fig. 2. Effect of mixture composition on apparent viscosity. Mixture B. (○) γ = 26,4 s^{-1}, (●) γ = 237,2 s^{-1}. t = 20 °C. Dashed line: Eq. (1). Solid line: Eq. (2).

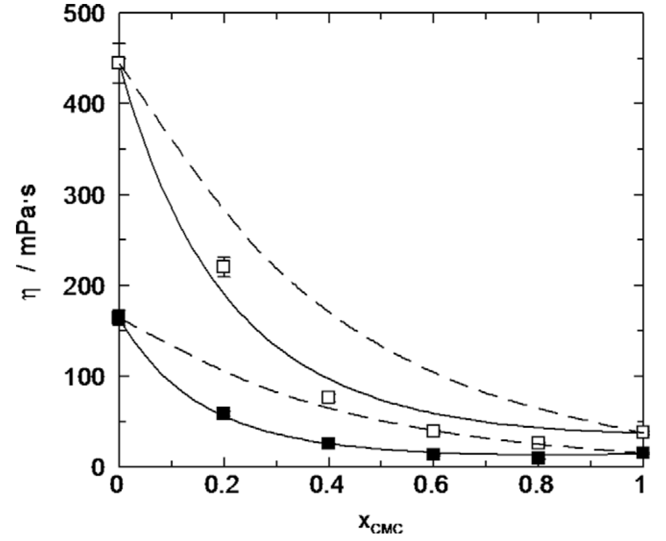

Fig. 3. Influence of mixture composition upon apparent viscosity. Mixture C. (□) t = 10 °C, (■) t = 50 °C. γ = 66 s^{-1}. Dashed line: Eq. (1). Solid line: Eq. (2).

The observed deviations from linearity, such us the observed behaviours in the present work, is due to different molecular interactions of polymer molecules in aqueous solutions (CMC and AG molecules in this work). Previous papers have detected similar deviations for other mixtures of polymers (Álvarez-Lorenzo et al., 2001; Gómez-Díaz et al., 2008b; Song et al., 2003). This effect has been observed for medium, high and low concentrations of poly-

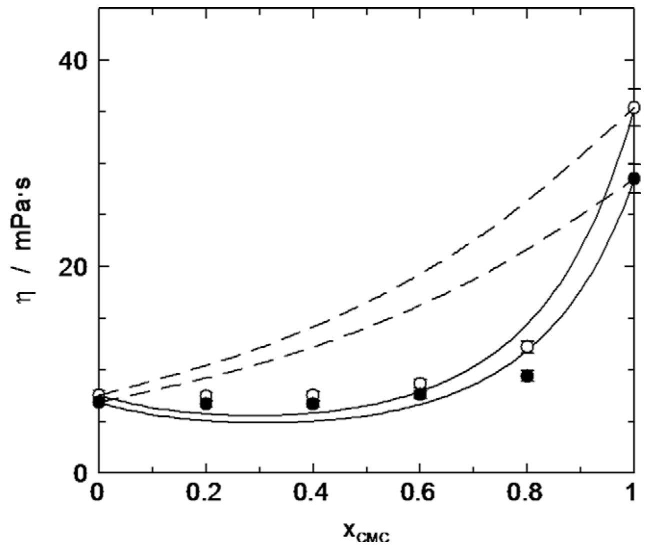

Fig. 4. Influence of mixture composition and shear rate upon apparent viscosity. Mixture E. t = 20 °C. (○) γ = 24,5 s^{-1}; (●) γ = 251 s^{-1}. Dashed line: Eq. (1). Solid line: Eq. (2).

mers, in a studied concentration range. For all the systems, negative deviations were observed producing minor value for intermediates values of polymer mixtures, that implies the existence of intermolecular interaction between carboxymethyl cellulose and Arabic gum polymers. The deviations were also more pronounced when the difference between compositions of the polymers blended dispersions is high.

The behaviour of these systems in water and in aqueous solutions of different NaCl concentration has been studied in order to evaluate the synergistic effect of the polymers mixtures employed in the present work. Fig. 5 shows an example of the experimental results obtained for the effect of electrolyte presence in the liquid mixture. For pure polymers aqueous solutions, an increase in NaCl in the solution produces a decrease in the viscosity. The decrease observed with the addition of NaCl is due to the charge screening of electrostatic repulsions and then, a more compact conformation is possible and it produces a decrease in the hydrodynamic size of the molecule, producing a decrease in viscosity (Khouryieh, Herald, Aramouni, & Alavi, 2007). Fig. 5 shows that an addition of 200 mM of NaCl to the polymers system produces a decrease in the synergistic interaction, whereas a non-synergistic interaction was observed when NaCl concentration was increased until 500 mM.

Different models have been employed in this work to fit the experimental data of apparent viscosity *versus* mixture composition. Several authors have used a log-additivity rule (Eq. (2)) for different polymers blends to fit the experimental data, taking into account the previously commented deviations.

$$\log \eta_{\mathrm{app}} = x_1 \cdot \log \eta_1 + x_2 \cdot \log \eta_2 \tag{2}$$

where x_1 and x_2 are the volume fraction and η_1, η_2, and η_{app} are the viscosity of aqueous solutions of individual polymers and the mixture viscosity, respectively.

Other model employed to fit the behaviour of this kind of systems is based on the introduction of one fit parameter. The equation obtained is the second order canonical model, and it adopts the expression shows in Eq. (3).

$$\log \eta_{\mathrm{app}} = x_1 \cdot \log \eta_1 + x_2 \cdot \log \eta_2 + x_1 \cdot x_2 \cdot \log \eta_{12} \tag{3}$$

where η_{12} was an adjustable parameter and the value of this parameter is related to the deviation from linearity (ideal behaviour). A value of unity of this parameter indicates an ideal behaviour.

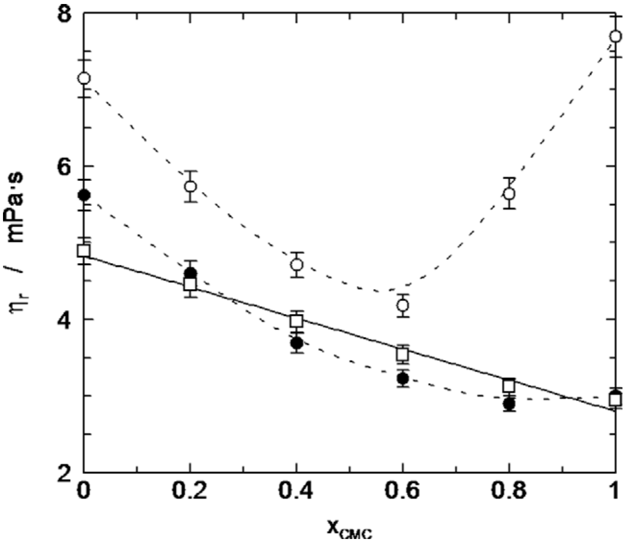

Fig. 5. Influence of NaCl presence upon apparent viscosity of mixtures of carboxymethyl cellulose + Arabic gum corresponding to mixtures A. (○) [NaCl] = 0 mM, (●) [NaCl] = 200 mM, (□) [NaCl] = 500 mM. $\gamma = 110\ \mathrm{s}^{-1}$. $t = 20\ ^{\circ}\mathrm{C}$.

Figs. 2–4 show the experimental values obtained for mixtures employed in the present study, and the fit contributed by the models previously presented (Eq. (2) – dashed line and Eq. (3) – solid line) at different mixtures conditions. The phenomenon observed in these figures is explained on the basis of a better spatial disposition of polymers chains due to interactions among polymers chains. A better spatial disposition improves the fluid flow when a decrease in viscosity is produced. Pal (1999) observed similar effects in other systems, such as suspensions and emulsions.

Taking into account the results shown in Figs. 2–4 we can conclude that Eq. (3), employed to fit the experimental results about the influence of composition upon viscosity, shows a suitable behaviour. Even thought the good behaviour shown by Eq. (3), one aim of this study consists in generalizing this equation for all the experimental conditions employed in this work (temperature, composition and applied shear rate). For this reason, a modification in Eq. (3) has been carried out. Previous studies (Song et al., 2003) has developed an important modification of Eq. (3) based on the addition of a extra-term with the aim of fitting the complex behaviour of Newtonian viscosity as regards composition of this kind of systems. The new equation implies the use of different fitting parameters obtained by the use of experimental data. The behaviour recommended by Song et al. (2003) implies the use of Newtonian viscosity (*vide supra*), that involves the use of other equations to determine the viscosity at high dilution or at elevate polymer concentration. This procedure implies an increase in the model complexity due to the use of an important number of equations.

In the present work we decided not to modify Eq. (3) and analyse the influence of experimental conditions upon the fit parameter, η_{12}. The analysis of different influences allows us to conclude that, for this system, temperature causes the most important effect upon the viscosity value. In relation to the influence of composition, it is included in the value of viscosity corresponding to individual polymer solutions (η_1 and η_2) due to the viscosity of each solution is related with the polymer concentration. On the other hand, the shear rate influence upon the fit parameter is considered low, and then, the influence of temperature upon fit parameter has only been taken into account. For these reasons, Eq. (4) has been developed to include in Eq. (3) in order to enhance the fit properties of the model.

$$\eta_{12} = \sum_{i=0}^{2} a_i \cdot t^i \tag{4}$$

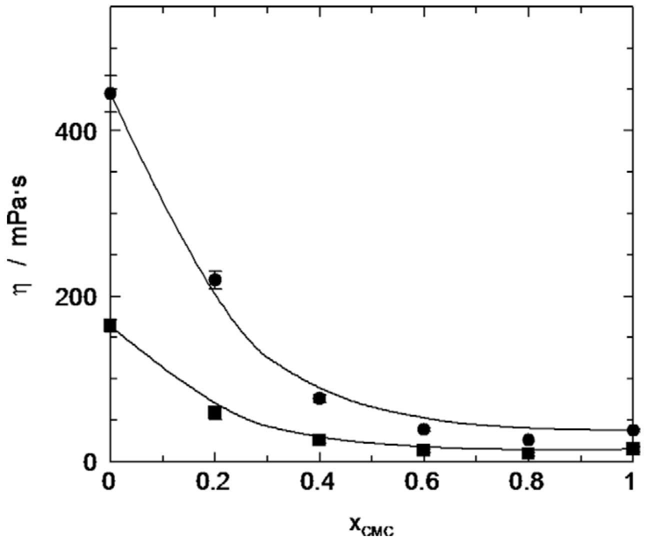

Fig. 6. Behaviour corresponds for model development based on Eqs. (2) and (3). Mixture C. (●) $t = 10\ ^{\circ}\mathrm{C}$, (■) $t = 50\ ^{\circ}\mathrm{C}$. $\gamma = 66\ \mathrm{s}^{-1}$.

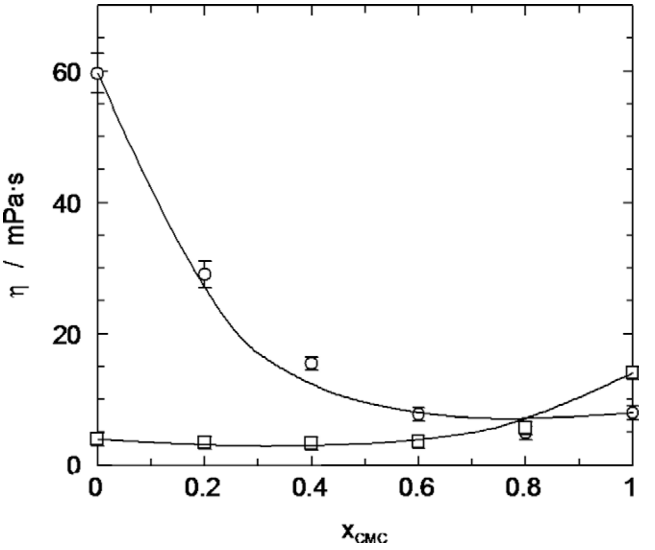

Fig. 7. Behaviour of the model based on Eqs. (2) and (3). t = 40 °C. γ = 220 s^{-1}. (○) Mixture B, (□) Mixture E.

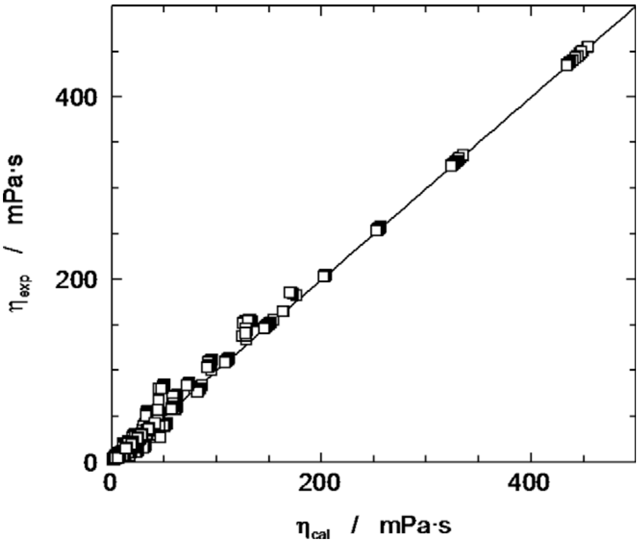

Fig. 8. Comparison of experimental apparent viscosity values and calculated ones using Eqs. (2) and (3).

where a_0, a_1 y a_2 are fit parameters. For the system analysed in the present work, and taking into account all experimental data obtained, medium values for fitting parameters corresponding to Eq. (4) have been obtained ($a_0 = 7.2 \times 10^{-2}$, $a_1 = -2.1 \times 10^{-3}$ and $a_2 = 2.5 \times 10^{-5}$).

Figs. 6 and 7 show different examples about the behaviour of the proposed model for the all the different experimental conditions employed we employed (composition/concentration, temperature and shear rate). In these figures it is possible to observe that the model allows us the calculation of the apparent viscosity values under different experimental conditions, with slight deviations regarding the experimental values. The results obtained, shown in Figs. 6 and 7, indicate that the model takes into account the influence of temperature and the kind of solutions in relation to polymers concentration.

Fig. 8 shows the global results in relation to the comparison of experimental values of apparent viscosity and the calculated ones by means of the model developed in this work. The results shown in Fig. 8 indicate that it fits satisfactorily the behaviour of aqueous solutions of mixtures of CMC and AG, with a standard deviation of 8 mPa s.

4. Conclusions

The rheological behaviour of aqueous solutions of polymers mixtures has been determined under different experimental conditions of composition, concentration, temperature and shear rate, and the experimental results show that these systems are included in the non-Newtonian and pseudoplastic fluids. Temperature and shear rate produce a decrease in the value of apparent viscosity. In relation to the composition effect, negative deviations from linear behaviour have been detected due to weak interaction between polymer molecules.

A new model has been employed to fit the influence of different experimental variables upon the apparent viscosity of these complex mixtures, and this model has shown suitable results.

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