

# Rheological behaviour of polysaccharide aqueous solutions

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## Abstract

Several data relative to the viscosity of water-soluble polysaccharide solutions were collected from the literature and processed by different rheological models. Some relationships between the viscosity of these polymer solutions, their molecular weight and their solution concentrations, were established and their validity checked. Thus, an accurate equation correlating the viscosity and both the shear rate and the solution concentration of different water soluble polysaccharides (xanthan, hyaluronan, carboxymethylcellulose) was deduced on the basis of Cross' model which suggests two domains in which the viscosity is constant, i.e. very low and very high shear rate ranges. Then, an expression relating the zero-shear viscosity ( $A$ ) and the concentration of their solutions was proposed. Finally, an alternative equation to that of Mark–Houwink correlating the molecular weight and the intrinsic viscosity of the water-soluble polysaccharides studied in this paper was found.

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## 1. Introduction

Polysaccharides are the most abundant organic polymers obtained by biosynthesis and available everywhere from different vegetal and animal sources and with a variety of structures. They have attracted many researchers because they present many advantages, namely: (i) their renewable character, (ii) their biodegradability, (iii) their relatively low cost and (iv) their easy conversion into different derivatives due to their reactivity towards many organic molecules. Apart the classical use of some of them, such cellulose molecules, as fibres in textile and papermaking, polysaccharides can be converted, or even directly available, as water-soluble polymers. This family has found useful applications in food hydrocolloids as witnesses the number of recent papers [1–20] and reviews [21–23] devoted to this field.

One of the most important property when using water-soluble polysaccharide as an additive in food formulation or cosmetics is the viscosity of their solution, which is a function of shear rate and depends, of course, on the molecular weights and the polymer concentration. Yamanaka and Mitsuishi [1] have studied such systems and proposed a model based on

combined forced and natural convective heat transfer from spheres to power-low fluids.

Then, Whitcomb and Macosko [2] have investigated the rheology of aqueous solutions of xanthan in a wide range of shear rate and found the xanthan solutions displayed a Newtonian behaviour at sufficient dilution and low shear rates. More concentrated solutions showed a yield stress. Although this work was focused on the conformational aspects and established that xanthan in solution is rodlike, having some flexibility, it gave also the rheological model describing the dilute and semi-dilute solutions (see below). Then, Milas et al. [3] investigated the viscosity dependence on concentration, molecular weight and shear rate of xanthan solutions with increasing the shear rate. They showed clearly that the xanthan solutions behave as Newtonian fluids at very low and very high shear rates and became rheo-thinning fluids in the intermediate range of shearing. They established, for dilute and semidilute solutions, a unique curve for the reduced specific viscosity as a function of the shear rate/critical shear rate ratio, for different molecular weight samples and polymer concentration. Finally, in this study a master curve correlating the specific viscosity and the overlap concentration was given.

Castelain et al. [4] have reported an investigation dealing with the study of the aqueous solutions of two carboxymethylcellulose samples with DS of 0.71 and 0.80, respectively, and hydroxyethylcellulose. They showed that Cross' model [24] was found to be the most adequate rheological expression fitting very well the experimental points. From this model

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### Nomenclature

$A$	‘hypothetic’ zero-shear solute viscosity, in Pa s	$\gamma$	dimensionless parameter of Eq. (15)
$A'$	‘hypothetic’ solute viscosity at infinite shear rate, in Pa s	$\eta$	viscosity of the solution, in Pa s
$A_0$	‘hypothetic’ zero-shear solute viscosity at zero-concentration, in Pa s	$\eta_c$	‘hypothetic’ viscosity of the solute
$B$	coefficient (Eq. (8)), in $s^{0.8}$	$\eta_0$	zero-shear viscosity of the solution, in Pa s
$C$	solution concentration, in $kg\ m^{-3}$ or $g\ L^{-1}$	$\eta_\infty$	viscosity of the solution at infinite shear rate, in Pa s
$\dot{\gamma}$	shear rate, in $s^{-1}$	$\eta_{rel}$	relative viscosity of the solution, dimensionless
$K$	coefficient (Eq. (1)), in $s^m$	$\eta_{sp}$	specific viscosity, dimensionless
$k$	coefficient of Eq. (11), in $Pa^{-1}$ and dimensionless parameter of Eq. (18)	$\eta_{sp,0}$	specific viscosity at zero-shear rate, dimensionless
$k_0$	coefficient of Eq. (13), in $Pa^{-1}$	$\eta_{red}$	reduced viscosity, in $L\ g^{-1}$ or $m^3\ kg^{-1}$
$M$	molecular weight, in $g\ mol^{-1}$	$\eta_{red,0}$	reduced viscosity at zero-shear rate, in $L\ g^{-1}$ or $m^3\ kg^{-1}$
$M_w$	weight-average molecular weight in $g\ mol^{-1}$	$[\eta]$	intrinsic viscosity of the solute, in $L\ g^{-1}$ or $m^3\ kg^{-1}$
$\bar{V}$	specific partial volume of the solute, in $m^3\ kg^{-1}$	$[\eta]_0$	intrinsic viscosity of the solute at zero-shear rate, in $L\ g^{-1}$ or $m^3\ kg^{-1}$
$V_0$	specific volume of the solute at zero-concentration	$\eta_s$	the solvent viscosity, in Pa s
$\varphi$	volume fraction of the solute (dimensionless)	$\tau$	shear stress, in Pa
$y$	dimensionless parameter of Eq. (11)	$a$	exponent of Mark Houwink relationship
$\alpha$	coefficient (Eq. (8)), in $s^{0.2}$ and dimensionless parameter of Eq. (15)	$N$	constant of Mark Houwink relationship
$\beta$	coefficient (Eq. (8)), in $s^{0.8}$ and dimensionless parameter of Eq. (15)	$x$	mass fraction
		$\rho$	density of the solution
		$\rho_0$	density of the solvent

the zero-shear viscosity is that measured at very low shear rate. They also established a correlation between the specific viscosity and the overlap concentration for the polysaccharides under study. Gravanis et al. [5] and Fouissac et al. [6] have studied a succinoglucan polysaccharide and hyaluronan, as a wormlike polyelectrolyte, in dilute and semi-dilute solutions and established the rheological parameters and the master curves reported before for the other polysaccharide.

In the last decade, food applications incited researcher undertaking investigation of different polysaccharides in view of their use as food additives. Among the polysaccharides studies, one can cite dextran [7], xanthan [9,16,18], hyaluronic and poly(galacturonic) acids in the sodium salt form [12,15], sodium alginates [13,19], exocellular polysaccharide produced by the bacterium *Latococcus lactis subsp. Cremonis B40* [14], gellan and galactomannan [18] and  $\beta$ -glucans [20].

Concerning the determination of the molecular weights of polymers, Mark–Houwink equation is used to assess this parameter, but it presents major drawbacks since it depends on the temperature, the solvent and the nature of the polymer under study. For the Newtonian flow range, the dependency of the viscosity on the concentration was also established for diluted and semi diluted solutions of cellulose derivatives, by building master curves involving the specific viscosity and the solution concentration [25].

The objective of the present paper is to collect literature data concerning different polysaccharide solutions and trying to establish general equations correlating these structural parameters.

## 2. Theoretical background

The studies chosen here to overview the effect of shear rate on the viscosity of aqueous polysaccharide solutions are those reported by Yamanaka and Mitsushishi [1], Sabiri [11], Ciceron [17] and Barba et al. [10] dealing with carboxymethylcellulose (CMC) and those of Milas et al. [3] investigating xanthans and Fouissac et al. [6] and Berriaud et al. [8] who studied hyaluronans. As mentioned above, the dilute solutions of cellulose derivatives can be reasonably described by Cross' model [24]:

$$\frac{\eta_0 - \eta}{\eta - \eta_\infty} = K(\dot{\gamma})^m \quad (1)$$

where  $\eta_0$  and  $\eta_\infty$  are the dynamic viscosity of the solution (Pa s) at very low and high shear rates, respectively;  $K$  ( $s^m$ ) and  $m$  constants parameters, generally called as consistency and flow index, respectively; and  $\dot{\gamma}$  the shear rate ( $s^{-1}$ ).

In Eq. (1),  $\eta$  represents the viscosity of solution which can be described as a function of the polymer concentration,  $C$ , considering an additivity relationship involving the solvent and the polymer phases contribution:

$$\eta = (1 - \varphi)\eta_s + \varphi\eta_c \quad (2)$$

where  $\varphi$  is the solute volume fraction,  $\eta_s$  the viscosity of the solvent and  $\eta_c$  is the contribution of the solute to the measured viscosity.  $\eta_c$  will be named ‘hypothetic’ viscosity of the pure solute.

The volume fraction,  $\phi$ , can also be expressed as:

$$\phi = C\bar{V}$$

where  $C$  is the solute concentration in  $\text{kg m}^{-3}$  (or  $\text{g L}^{-1}$ ) and  $\bar{V}$  specific partial volume of the solute, in  $\text{m}^3 \text{kg}^{-1}$ .

The volume fraction can also be expressed as a function of mass fraction,  $x$ , according to the following equation:

$$\phi = 1 - (1-x) \frac{\rho}{\rho_0}$$

where  $\rho$  and  $\rho_0$  are the density of the solution and that of the solvent, respectively.

Now if one considers that  $\eta_c$  is the viscosity of the solute, which depends on the  $C$  and the shear rate,  $\dot{\gamma}$ , then,  $\eta_c$  can be related the  $\phi$  and  $\eta$ , according to:

$$\eta_c = \frac{\eta - (1-\phi)\eta_s}{\phi} \quad (3)$$

Then, if one takes the following notations:  $\eta_{c,\infty} = A'$  and  $\eta_{c,0} = A$  Cross model becomes:

$$\frac{A - \eta_c}{\eta_c - A'} = K(\dot{\gamma})^m \quad (1a)$$

which can also be written as:

$$\eta_c = \frac{A}{1 + \left[ \frac{(1 - \frac{A'}{A})K(\dot{\gamma})^m}{1 + (\frac{A'}{A})K(\dot{\gamma})^m} \right]}$$

or

$$\eta_c = \frac{A}{1 + \left[ \frac{B(\dot{\gamma})^m}{1 + \beta(\dot{\gamma})^m} \right]} \quad (3a)$$

if

$$B = \left(1 - \frac{A'}{A}\right)K$$

$$\beta = \left(\frac{A'}{A}\right)K$$

The increment of relative viscosity, called also as specific viscosity, can be defined as:

$$\eta_{sp} = \frac{\eta}{\eta_s} - 1 \quad (4)$$

Combining Eqs. (1) and (4), the Expression (4a) can be obtained:

$$\eta_{sp} = \phi \left( \frac{\eta_c}{\eta_s} - 1 \right) \quad (4a)$$

and the reduced viscosity,  $\eta_{red}$ , can be defined as:

$$\eta_{red} = \frac{\eta_{sp}}{C} \quad (5)$$

or by:

$$\eta_{red} = \bar{V} \left( \frac{\eta_c}{\eta_s} - 1 \right) \quad (5a)$$

In the zero-shear rate conditions, in which the fluid obeys to Newtonian law, the reduced viscosity can be expressed:

$$\eta_{red} \dot{\gamma} \rightarrow 0 = \bar{V} \left( \frac{A}{\eta_s} - 1 \right) \quad (6)$$

When the concentration of the solute tends to zero, the limit value of the reduced viscosity is called intrinsic viscosity  $[\eta]$ . At zero-shear rate  $[\eta]$  tends also to a limit value  $[\eta]_0$ , which can be described as:

$$[\eta]_0 = V_0 \left( \frac{A_0}{\eta_s} - 1 \right) \quad (7)$$

where  $V_0$  is the specific volume of the solute at infinite dilution and  $A_0$  its hypothetical viscosity in the Newtonian regime, obtained by extrapolation to infinite dilution conditions.

### 3. The viscosity of the solute as a function of the shear rate

Milas et al. [3] have studied the rheological behaviour of xanthan solutions as a function of molecular weight and concentration of the polymer. Their results obeyed to the following Eq. (8), which contains different parameters. Eq. (8) can be derived from Expression (3a):

$$\eta_c = \frac{A[1 + \alpha(\dot{\gamma})^{0.2}]}{1 + \left[ \frac{B(\dot{\gamma})^{0.8}}{1 + \beta(\dot{\gamma})^{0.8}} \right]} \quad (8)$$

Table 1 summarizes the values, obtained by processing different data collected in the literature, of the four coefficients  $\alpha$ ,  $A$ ,  $B$  and  $\beta$ , as well as that of the ratio  $A/A'$  (where  $A/A' = (B + \beta)/\beta$ ) and that of  $K$  ( $K = B + \beta$ ). In this Table the values of the correlations between the measured and the calculated viscosity are listed. From Table 1, different concluding remarks could be drawn.

- (i) There is very good agreement between the values of the correlation between the measured and the calculated viscosity.
- (ii) The values of parameter  $K$  as well as those of the hypothetical viscosity of the pure solute,  $A$ , decreased with decreasing the solution concentration, whereas the dependence of  $A'$  with the solution concentration was found to be a function of the solute used.
- (iii) The experiments made using CMC showed that for highly concentrated solution under high shear rates, the  $B$  coefficient depended strongly on  $\dot{\gamma}$ .
- (iv) These data show that the CMC solutions studied by Sabiri [11] and Ciceron [17] behaved very closely to CMC A used by Barba et al. [18], whereas the CMC B studied by the later displayed much lower viscosity. Finally, the CMC investigated by Yamanaka [1] was found to have an intermediate behaviour.

Table 1

The values of the four coefficients  $\alpha$ ,  $A$ ,  $B$  and  $\beta$ , collected in the literature and allowing the establishment of the expression of the viscosity as a function of shear rate and concentration (Eq. (8))

Polysaccharide derivative	$M_w$	$C$ (g L <sup>-1</sup> )	$\alpha$ (s <sup>0.2</sup> )	$A$ (Pa s)	$\beta \times 10^3$ (s <sup>0.8</sup> )	$B$ (s <sup>0.8</sup> )	$A/A'$	$K$ (s <sup>0.8</sup> )	Correlation coefficient	Ref.
Xanthan	$7.0 \times 10^6$	2.0	0.035	5800	1.9	7.60	4160	7.60	$1.005 \pm 0.033$	[3]
		1.5	0.038	1900	2.8	2.94	1050	2.94	$0.995 \pm 0.057$	
		1.0	0.043	530	4.15	0.996	241	1.00	$0.992 \pm 0.078$	
		0.5	0.054	109	6.1	0.226	38	0.232	$0.999 \pm 0.064$	
		0.25	0.070	40	7.4	$7.18 \times 10^{-2}$	10.7	$7.92 \times 10^{-2}$	$0.999 \pm 0.048$	
		0.125	0.097	21.5	8.15	$2.85 \times 10^{-2}$	4.5	$3.67 \times 10^{-2}$	$1.010 \pm 0.035$	
		0.0625	0.319	14.5	8.55	$3.08 \times 10^{-2}$	4.6	$3.94 \times 10^{-2}$	$1.002 \pm 0.020$	
	$7.0 \times 10^6$	2.0	0.035	5800	1.90	6.70	4160	6.70	$1.005 \pm 0.033$	
	$5.3 \times 10^6$		0.040	1180		2.00	1050	2.00	$0.997 \pm 0.035$	
	$2.2 \times 10^6$		0.062	22		$4.75 \times 10^{-2}$	26.0	$4.94 \times 10^{-2}$	$1.010 \pm 0.058$	
	$1.0 \times 10^6$		0.092	3.45		$5.78 \times 10^{-3}$	4.0	$7.60 \times 10^{-3}$	$1.000 \pm 0.086$	
	$4.5 \times 10^5$		0.137	0.68		$\approx 0$	$\approx 1$	$\approx 1.90 \times 10^{-3}$	$1.004 \pm 0.020$	
	$3.1 \times 10^5$		0.165	0.39		$\approx 0$	$\approx 1$	$\approx 1.90 \times 10^{-3}$	$0.095 \pm 0.030$	
	Hyaluronan	$1.3 \times 10^6$	9.68	$\approx 0$	367	$\approx 0$	0.12	$\approx \infty$	0.12	
14.67				1980		0.33		0.33	$1.001 \pm 0.037$	
24.12				9360		0.66		0.66	$0.993 \pm 0.061$	
33.92				28500		1.5		1.5	$1.011 \pm 0.115$	
56.7				88200		2.6		2.6	$0.992 \pm 0.033$	
83				253000		5.9		5.9	$0.991 \pm 0.020$	
CMC A		5	$\approx 0$	30.1	0.460	1.54	4.35	2.00	$1.000 \pm 0.178$	[10]
		12		61.6	0.155	0.505	4.26	0.66	$1.000 \pm 0.137$	
		20		1540	0.061	2.12	35.8	2.18	$1.000 \pm 0.086$	
		30		21400	0.049	11.8	2.42	11.80	$1.002 \pm 0.120$	
		40		138000	0.040	48.0	1.2	48.0	$0.998 \pm 0.122$	
		50		200000	0.040	46.9	1.17	46.90	$0.998 \pm 0.161$	
CMC B		7	$\approx 0$	$\approx 2.5$	$1.5 \times 10^{-3}$	–	$\dot{\gamma}/5.0$	$\dot{\gamma}/5.0$	$1.000 \pm 0.088$	[10]
		15		4.57		$1.80 \times 10^{-3}$		$3.30 \times 10^{-3}$	$1.000 \pm 0.011$	
		20		7.97		$4.00 \times 10^{-3}$			$1.000 \pm 0.025$	
		31		19.7		$7.65 \times 10^{-3}$			$1.001 \pm 0.062$	
		50		83.6		$2.20 \times 10^{-2}$			$1.000 \pm 0.033$	
		100		593		$8.2 \times 10^{-2}$			$1.000 \pm 0.006$	
		150		1970		$\exp(\dot{\gamma}/208)$			$0.995 \pm 0.095$	
		200		9250		$0.25 \exp(\dot{\gamma}/39)$			$0.994 \pm 0.054$	
CMC		6		16.2	$185 \times 10^{-3}$	$1.15 \times 10^{-2}$	7.22	$1.34 \times 10^{-2}$	$1.000 \pm 0.030$	[11]
CMC		55.2		1650	1.98	0.997	1.49	2.96	$1.000 \pm 0.005$	[1]
CMC		6		13.7	$1.02 \times 10^{-3}$	$7.63 \times 10^{-3}$	8.48	$8.65 \times 10^{-3}$	$1.000 \pm 0.016$	[17]
		6	$\approx 0$	15.1	$1.56 \times 10^{-3}$	$1.04 \times 10^{-2}$	7.67	$1.20 \times 10^{-2}$	$1.000 \pm 0.039$	
		6		12.1	$1.30 \times 10^{-3}$	$9.00 \times 10^{-3}$	7.92	$1.03 \times 10^{-2}$	$0.999 \pm 0.040$	
		8		29.7	$1.40 \times 10^{-3}$	$1.65 \times 10^{-2}$	12.8	$1.79 \times 10^{-2}$	$0.999 \pm 0.021$	
		8		48.5	$1.55 \times 10^{-3}$	$2.60 \times 10^{-2}$	17.8	$2.76 \times 10^{-2}$	$0.999 \pm 0.027$	
8		37.1		$1.8 \times 10^{-3}$	$2.15 \times 10^{-2}$	12.9	$2.33 \times 10^{-2}$	$1.002 \pm 0.034$		

The Cross' model describes quite well the behaviour of different solutions, but presents the drawback consisting on the absence of any physical meaning which could be attributed to  $K$  and  $m$  parameters. That is why, it was decided to express the  $\eta_s$  as a function of shear stress  $\tau = \eta \dot{\gamma}$  rather than shear rate ( $\dot{\gamma}$ ).

The interest of working with  $\tau$  resides on its much more direct action on the organization and the flowing behaviour of

the macromolecules inside the solution. Knowing that, the viscosity of the solution at extreme values of shear rates is constant we shall write:

$$\eta_c = A^y A'^{1-y} \quad (9)$$

In Eq. (9),  $y$  is a function of shear stress  $\tau$  and can be identified varying the  $\eta_c$  as a function of  $\tau$ , as follows:

$$\ln \eta_c = \ln A' + y \ln \left( \frac{A}{A'} \right) \quad (10)$$

If one excludes the highly concentrated solutions of CMC tested at high values of shear rates where the  $K$  parameter of Cross' model is a function of  $\dot{\gamma}$ , the parameter  $y$  can be expressed as:

$$y = \exp -k\tau \quad (11)$$

For the low values of  $k\tau$ , the limit form of  $y$  is:

$$y = 1 - k\tau$$

which gives:

$$\ln \eta_c = \ln A - k\tau \ln \frac{A}{A'} \quad (12)$$

Table 2 summarizes the values of  $A$ ,  $A'$  and  $k$  identified from the experimental data relatives to the solutions studied. It is

worth noting that for the hyaluronan solutions having  $M_w$  of  $1.3 \times 10^6$ , the values of  $k$  could not be identified because the  $A'/A$  ratio was close to zero. This corroborates with processing the experimental data according to Cross' model. Moreover, for diluted solutions of CMC B, the  $A$  and  $A'$  values are very similar. In fact, they are quasi-equal at  $C=7$  and  $15 \text{ g L}^{-1}$ , which made impossible the identification of  $A'$  from Eq. (10). The  $A$  values given in Tables 1 and 2 are not always close, since their ratio is 1.28, 1.00, 1.67, 1.00 and 0.95, respectively for xanthan, hyaluronan, CMC A, CMC B and Sabiri' and Ciceron's CMC. The quite high difference between the values of  $A$  for xanthan solutions is probably due to the fact that contrary to Eq. (9), expression (8) takes into account the slight rheo-thickening effect of these solutions at low shear rates. The second very different value concerns CMC A solutions and could be attributed to relatively high dispersion of the experimental data.

Table 2

The values of the three coefficients  $A$ ,  $A'$  and  $k$ , collected in the literature and allowing the establishment of the expression of the viscosity as a function of shear rate and concentration where:  $C$  is the solute concentration in  $\text{kg m}^{-3}$ ,  $M_w$  the weight average molecular weight in  $\text{g mol}^{-1}$  and  $\varphi$  the volume fraction of the solute.

Polysaccharide derivative	$M_w$	$C \text{ g L}^{-1}$	$\varphi$	$A \text{ Pa s}$	$A' \text{ Pa s}$	$K$	$k \ln(A/A')$	Correlation coefficient	Ref.	
Xanthan	$7.0 \times 10^6$	2.0	$1.24 \times 10^{-3}$	6865	3.324	0.342	–	$0.967 \pm 0.175$	[3]	
		1.5	$9.10 \times 10^{-4}$	2193	4.419	0.524	–	$1.007 \pm 0.104$		
		1.0	$6.20 \times 10^{-4}$	634.0	4.754	0.854	–	$1.012 \pm 0.077$		
		0.5	$3.10 \times 10^{-4}$	110.9	5.144	1.271	–	$1.022 \pm 0.121$		
		0.25	$1.55 \times 10^{-4}$	49.08	6.563	2.413	–	$0.983 \pm 0.079$		
		0.125	$7.75 \times 10^{-5}$	27.80	8.735	3.640	–	$1.000 \pm 0.015$		
		0.0625	$3.875 \times 10^{-5}$	24.80	8.376	6.125	–	$1.003 \pm 0.031$		
		2.0	$1.24 \times 10^{-3}$	6865	3.324	0.342	–	$0.967 \pm 0.175$		
		$5.3 \times 10^6$		1480	3.05	0.459	–	$1.012 \pm 0.077$		
		$2.2 \times 10^6$		29	1.88	0.306	–	$1.001 \pm 0.051$		
Hyaluronan	$1.3 \times 10^6$	83	$5.15 \times 10^{-2}$	$2.58 \times 10^5$	–	–	$9.90 \times 10^{-4}$	$0.998 \pm 0.030$	[8]	
		56.7	$3.52 \times 10^{-2}$	$9.56 \times 10^4$	–	–	$1.49 \times 10^{-3}$	$1.001 \pm 0.039$		
		33.92	$2.10 \times 10^{-2}$	$2.73 \times 10^4$	–	–	$2.73 \times 10^{-3}$	$1.001 \pm 0.041$		
		24.12	$1.50 \times 10^{-2}$	$9.45 \times 10^3$	–	–	$5.12 \times 10^{-3}$	$0.996 \pm 0.008$		
		14.67	$9.10 \times 10^{-3}$	$1.90 \times 10^2$	–	–	$1.77 \times 10^{-2}$	$0.957 \pm 0.087$		
		9.28	$6.00 \times 10^{-3}$	351	–	–	$3.89 \times 10^{-2}$	$1.036 \pm 0.098$		
		5	$3.10 \times 10^{-3}$	17.1	7.60	8.34	–	$1.004 \pm 0.105$		
CMC A	100	100	$6.20 \times 10^{-2}$	$4.36 \times 10^6$	11500	$2.13 \times 10^{-3}$	–	$1.002 \pm 0.055$	[10]	
		50	$3.10 \times 10^{-2}$	$6.07 \times 10^5$	747	$1.00 \times 10^{-2}$	–	$1.008 \pm 0.245$		
		30	$1.86 \times 10^{-2}$	$3.71 \times 10^4$	326	$3.49 \times 10^{-2}$	–	$0.994 \pm 0.345$		
		20	$1.24 \times 10^{-2}$	$1.97 \times 10^3$	78	$9.75 \times 10^{-2}$	–	$0.994 \pm 0.173$		
		10	$6.2 \times 10^{-3}$	59.7	17.40	1.14	–	$1.007 \pm 0.125$		
		5	$3.10 \times 10^{-3}$	17.1	7.60	8.34	–	$1.004 \pm 0.105$		
		200	$1.24 \times 10^{-1}$	$8.82 \times 10^3$	–	–	$1.23 \times 10^{-3}$	$1.001 \pm 0.034$		[10]
		150	$9.30 \times 10^{-2}$	$1.96 \times 10^3$	–	–	$1.66 \times 10^{-3}$	$1.001 \pm 0.048$		
CMC B	100	100	$6.20 \times 10^{-2}$	588	163	$1.65 \times 10^{-3}$	–	$1.000 \pm 0.003$	[10]	
		50	$3.10 \times 10^{-2}$	85.2	65.8	$7.47 \times 10^{-2}$	–	$1.001 \pm 0.047$		
		31	$1.92 \times 10^{-2}$	19.6	16.8	0.40	–	$1.023 \pm 0.229$		
		20	$1.24 \times 10^{-2}$	8.79	7.28	1.117	–	$1.000 \pm 0.042$		
		15	$9.30 \times 10^{-3}$	4.45	–	–	$8.28 \times 10^{-3}$	$1.000 \pm 0.009$		
		7	$4.33 \times 10^{-3}$	2.49	–	–	–	$1.000 \pm 0.082$		[10]
		8	$4.96 \times 10^{-3}$	29.13	2.70	$2.37 \times 10^{-2}$	–	$1.000 \pm 0.021$		
		CMC	8			47.7	4.40	$2.89 \times 10^{-2}$		–
				36.1	2.45	$2.11 \times 10^{-2}$	–	$1.002 \pm 0.034$		
6	$3.72 \times 10^{-3}$			25.1	3.28	$6.18 \times 10^{-2}$	–	$1.003 \pm 0.074$		
				10.6	2.81	$9.50 \times 10^{-2}$	–	$1.007 \pm 0.126$		
				12.5	3.30	$9.00 \times 10^{-2}$	–	$1.004 \pm 0.076$		
				–	–	–	–	–		
				–	–	–	–	–		
CMC	–	55.2	$3.42 \times 10^{-2}$	–	–	–	–	[1]		
CMC	–	6	$3.72 \times 10^{-3}$	14.53	2.95	$4.92 \times 10^{-2}$	–	$1.000 \pm 0.025$	[11]	

From the data collected in Table 2 one can observe that the  $A$  and  $A'$  values become close for diluted solutions. Extrapolating these values to  $C=0$ , which corresponds to the Newtonian behaviour of the solutions under study, i.e.  $\eta_c=A=A'$ , then, it can be deduced that  $A' \rightarrow A_0$ . The other trend in these values concerns those of parameter  $k$ , which increases with decreasing  $C$ . It then appeared that for a given shear stress, the contribution of  $A'$  for the determination of  $\eta_c$ , increases with decreasing  $C$ . Of course the parameter  $A$  behaves in inverse trend. Since this contribution is higher for higher values of  $\tau$ , it can be deduced that for diluted systems,  $\eta_c \approx A'$  is always verified, which is in agreement with a Newtonian behaviour of the solutions under study in the described conditions.

In conclusion, the combination of Eqs. (9) and (11) gives rise to an acceptable representation of the variation of  $\eta_c$ , calling upon the identification of three parameters  $A$ ,  $A'$  and  $k$ , with invariable dimensions. Thus, an alternative to Cross' equation can be given (necessitating the identification of four parameters  $A$ ,  $A'$ ,  $K$  and  $m$ , (with  $K$  having variable dimensions expressed in  $s^m$ ). Nevertheless, the use of Cross' model remain actual, because processing the data using the three parameter model proposed here requires experimental data within a wide

range of shear stress ( $\tau$ ), in order to have different values between the expression  $\exp(-k\tau)$  and its limit form  $1-k\tau$ .

The  $k$  values of xanthan and CMC solutions summarized in Table 2, can be correlated according to the following empirical equation:

$$k = \frac{k_0}{\sinh[80\{1 + \exp(-1330\phi^2)\}\phi^{2/3}]} \quad (13)$$

where  $k_0$  is a parameter expressed in  $\text{Pa}^{-1}$  and describing the sensitivity of the solution to the shear stress ( $\tau$ ) effect.

$$\begin{aligned} \text{Xanthan}(M_w=7 \times 10^6) &\rightarrow k_0 = 1.11 \pm 0.07 \text{ Pa}^{-1} \\ \text{CMC A}(C \leq 50 \text{ g L}^{-1}) &\rightarrow k_0 = 124 \pm 22 \text{ Pa}^{-1} \\ \text{CMC B}(C \leq 50 \text{ g L}^{-1}) &\rightarrow k_0 = 1440 \pm 600 \text{ Pa}^{-1} \\ \text{CMC of Sabiri [11] and Ciceron [17]} &\rightarrow k_0 = 1.46 \pm 0.44 \text{ Pa}^{-1} \end{aligned}$$

Fig. 1 shows the correlation between the experimental values and those predicted from Expression (9), (11) and (13), for the solutions of the CMC A [12] (Fig. 1(a)) and those relating to xanthan ( $M_w=7 \times 10^6$ ) counterpart [3] (Fig. 1(b)). It is worth noting that: (i) for solution with  $C=100 \text{ g L}^{-1}$ , in order to get a good fit between experimental and calculated values, one should use a value of  $k_0$  of 318, instead of 124 and (ii) the viscosities measured for solutions with  $C > 20 \text{ g L}^{-1}$  at high shear rates ( $\dot{\gamma}$ ) are systematically lower than those calculated. Fig. 2 shows the shear stress–shear rate dependence of CMC A solutions with  $C=50$  and  $100 \text{ g L}^{-1}$ . This figure illustrates that the calculated and experimental curves of shear stress–shear rate dependence are very close to each other for both concentrations and for low values of shear rates, i.e. lower than 10 and  $1 \text{ s}^{-1}$ , for  $C=50$  and  $100 \text{ g L}^{-1}$ , respectively. This artefact could be associated to the perturbation of the swollen deformable aggregates in the solution under high shear rate and high concentrations. In fact for lower concentrations ( $C=10$  and  $20 \text{ g L}^{-1}$ ), this phenomenon was not observed. Work is in progress to elucidate this artefact.

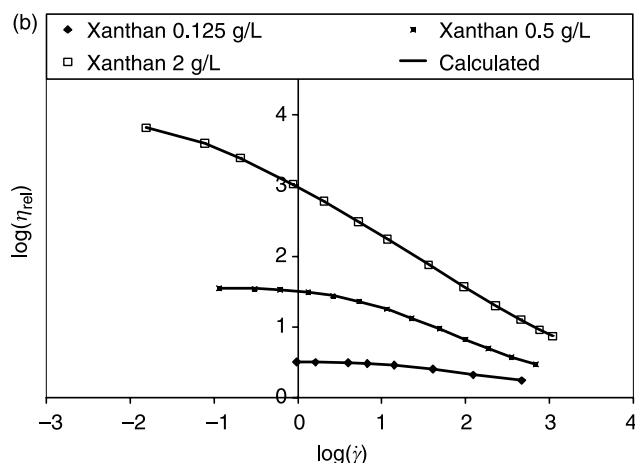
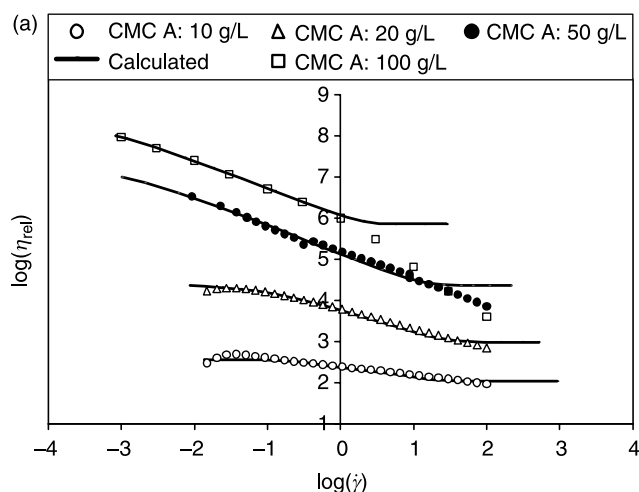


Fig. 1.  $\log\text{-}\log(\eta_{\text{rel}})$  versus shear rate ( $\dot{\gamma}$ ): comparison between calculated and measured values for CMC A (a) and xanthan with  $M_w=7 \times 10^6 \text{ g mol}^{-1}$  (b) solutions.

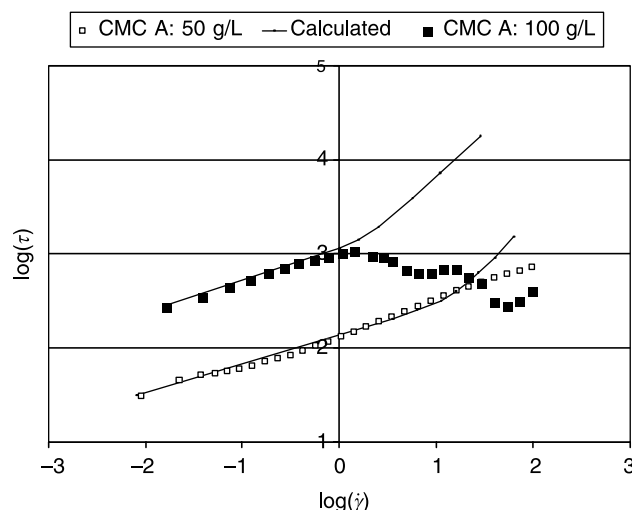


Fig. 2.  $\log(\tau)$  versus  $\log(\dot{\gamma})$  for CMC A solutions with concentrations of 50 and  $100 \text{ g L}^{-1}$ .

#### 4. The viscosity of the solute in the Newtonian regime and as a function of concentration

##### 4.1. Model purely Newtonian liquids: glycerol–water system

Glycerol is a polyol presenting the same interactions with water as those arising from polysaccharides when dissolved in aqueous media, except the fact that it is much smaller in terms of the molecule size and too stiff, such way that it cannot be deformed and consequently its solutions in water do not display any rheo-thinning behaviour.

Starting from the literature data taken from handbook of Chemistry and Physics [25], we calculated the ‘hypothetic’ viscosity of the pure solute for a full range of concentrations, as summarized in Table 3 and using the following equations:

$$C = x\rho$$

$$\varphi = 1 - (1 - x) \left( \frac{\rho}{\rho_0} \right)$$

$$\bar{V} = \frac{\varphi}{C}$$

$$A = \frac{\eta - (1 - \varphi)\eta_s}{\varphi}$$

From these data, it can be observed that:

- (i)  $\bar{V}$  varies only very slightly with the concentration and its value at zero-concentration was found to be about  $7.66 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1}$  [25].
- (ii)  $A_0$  can be estimated to 4.44 mPa s.

- (iii) The intrinsic viscosity, for glycerol at 20 °C, is around  $2.62 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ , (Eq. 7).
- (iv)  $A$  as a function of volume fraction of the solute can be expressed using the following empirical equation:

$$\ln \frac{A}{A_0} = 0.380[1 - \exp(63.840\varphi)]\exp(2.742\varphi) \quad (14)$$

The values of the solution viscosity, calculated using Eqs. (2) and (14) are reported in the last columns of Table 3. Very good correlation between these values and those measured was found, i.e.:

$$\eta = (1.000 \pm 0.009)\eta_{\text{calc}}$$

##### 4.2. Rheo-thinning fluids: hyaluronan-based solutions

The viscosity of the solutions of hyaluronan with different molecular weights, at 25 °C, was studied by Fouissac et al. [6] and Berriaud et al. [8]. They presented the results obtained in the following form:

$$\log \eta_{\text{sp}} = f(\log C)$$

Assuming there is no large difference between dried and swollen state, and knowing that the specific volume of polysaccharides is  $V_0 = 6.2 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1}$ , it follows that  $\varphi = 6.2 \times 10^{-4} C$ . On the other hand, the Eq. (4a) gives rise to the value of  $A$  (the hypothetic viscosity of the pure solute at low shear rate), as:

$$A = \eta_c \left[ \frac{\eta_{\text{sp}}}{\varphi} + 1 \right] \quad (14a)$$

Thus, regardless the molecular weight of the solute, the variation of  $A$  as a function of  $\varphi$  can be expressed by an

Table 3  
Characteristic values of aqueous solutions of glycerol at 20 °C

$X$	$\eta$ (Pa s)	$\rho$ (kg m <sup>-3</sup> )	$C$ (kg m <sup>-3</sup> )	$\varphi$	$\bar{V} 10^{-4} \text{ m}^3 \text{ kg}^{-1}$	$A$ (Pa s)	$\eta_{\text{calc}}$ (Pa s)
0	$1.005 \times 10^{-3}$	998.2	0.00	0.0000	7.660	$4.440 \times 10^{-3}$	$1.005 \times 10^{-3}$
0.1	$1.31 \times 10^{-3}$	1022.1	102.21	0.0785	7.675	$4.893 \times 10^{-3}$	$1.320 \times 10^{-3}$
0.2	$1.76 \times 10^{-3}$	1047	209.40	0.1609	7.683	$5.698 \times 10^{-3}$	$1.7681 \times 10^{-3}$
0.3	$2.50 \times 10^{-3}$	1072.7	321.81	0.2478	7.699	$7.039 \times 10^{-3}$	$2.499 \times 10^{-3}$
0.4	$3.72 \times 10^{-3}$	1099.5	439.80	0.3391	7.711	$9.011 \times 10^{-3}$	$3.699 \times 10^{-3}$
0.5	$6.00 \times 10^{-3}$	1126.3	563.15	0.4358	7.739	$1.247 \times 10^{-2}$	$5.932 \times 10^{-3}$
0.6	$1.08 \times 10^{-2}$	1153.3	691.98	0.5378	7.773	$1.922 \times 10^{-2}$	$1.064 \times 10^{-2}$
0.65	$1.52 \times 10^{-2}$	1167	758.55	0.5908	7.789	$2.503 \times 10^{-2}$	$1.508 \times 10^{-2}$
0.7	$2.25 \times 10^{-2}$	1180.8	826.56	0.6451	7.805	$3.432 \times 10^{-2}$	$2.241 \times 10^{-2}$
0.75	$3.55 \times 10^{-2}$	1194.4	895.80	0.7009	7.824	$5.023 \times 10^{-2}$	$3.533 \times 10^{-2}$
0.8	$6.01 \times 10^{-2}$	1207.9	966.32	0.7580	7.844	$7.897 \times 10^{-2}$	$5.970 \times 10^{-2}$
0.85	0.109	1221.4	1038.19	0.8165	7.864	0.1333	0.1099
0.9	0.219	1234.7	1111.23	0.8763	7.886	0.2498	0.2247
0.91	0.259	1237.4	1126.03	0.8884	7.890	0.2914	0.2629
0.92	0.31	1240.1	1140.89	0.9006	7.894	0.3441	0.3095
0.93	0.367	1242.8	1155.80	0.9128	7.898	0.4019	0.3641
0.94	0.437	1245.5	1170.77	0.9251	7.902	0.4723	0.4359
0.95	0.523	1248.2	1185.79	0.9375	7.906	0.5578	0.5225
0.96	0.624	1250.8	1200.77	0.9499	7.911	0.6569	0.6298
0.97	0.765	1253.4	1215.80	0.9623	7.915	0.7949	0.7635
0.98	0.939	1255.9	1230.78	0.9748	7.920	0.9632	0.9326
0.99	1.150	1258.4	1245.82	0.9874	7.926	1.1647	1.1483
1	1.412	1260.9	1260.90	1.0000	7.931	1.4120	1.4233

Table 4  
The values of the parameters obtained, by processing the literature data

Authors	$M_w$	$A_0$ (Pa s)	$\alpha$	$\beta$	$\gamma$	$\eta_{sp}$ meas./ $\eta_{sp}$ calc.
[8]	$2.0 \times 10^6$	6.980	8.50	240	9.0	$1.000 \pm 0.146$
	$1.3 \times 10^6$	3.422	8.50	143	5.6	$1.000 \pm 0.094$
	$8.0 \times 10^5$	2.700	8.50	97	4.4	$1.000 \pm 0.097$
	$3.0 \times 10^5$	1.015	8.50	38.5	0.5	$1.000 \pm 0.098$
[6]	$2.2 \times 10^6$	5.215	8.50	206	10	$1.000 \pm 0.147$
	$1.0 \times 10^6$	3.205	8.50	110	5	$1.000 \pm 0.098$
	$3.5 \times 10^5$	1.141	8.50	37	1	$1.000 \pm 0.177$

expression, similar to Eq. (14):

$$\ln \frac{A}{A_0} = \alpha[1 - \exp(-\beta\phi)]\exp(\gamma\phi) \quad (15)$$

For very low values of  $\phi$ , the limit value of Eq. (15) is:

$$\ln A = \ln A_0 + \alpha\beta\phi \quad (15a)$$

Then, it is possible to deduce the values of  $A_0$  for each solute.

Table 4 summarizes the values of  $A_0$ ,  $\alpha$ ,  $\beta$  and  $\gamma$  identified from the experimental data reported by Fouissac et al. [6] and Berriaud et al. [8]. The last column of Table 4 indicates the correlation between the values of  $\eta_{sp}$  measured and calculated using Eqs. (14a) and (15).

From these data one can conclude that Eq. (15) fits very well the experimental data for the concentrations varying from 0.1 to 100 g L<sup>-1</sup> (for which  $\eta_{sp}$  values range from 0.2 to  $4 \times 10^7$ ). It is also worth noting that  $\alpha$  coefficient is molecular weight independent and seems therefore to be associated to the chemical structure of the solute. On the hand, the values of  $A_0$ , which were obtained by extrapolation of  $\ln A$  to  $\phi=0$ , allowed the deduction of the limit intrinsic viscosity  $[\eta]_0$ , which can be compared to the data obtained by Berriaud and Fouissac [6,8], as summarized in Table 5. Except for  $M=2.0 \times 10^6$ , the ratio between the limit intrinsic viscosity  $[\eta]_0$  obtained by Berriaud and Fouissac and that deduced from relation (7) are very close. In fact, it is easy to deduce the following equation:

$$[\eta]_0 = (0.995 \pm 0.060) \left[ V_0 \left( \frac{A_0}{\eta_s} - 1 \right) \right]$$

Table 5  
The values of  $A_0$  and that of deduced limit intrinsic viscosity  $[\eta]_0$

References	$M_w$	$[\eta]_0$ L/g from literature	$[\eta]_0 = V_0 \left( \frac{A_0}{\eta_s} - 1 \right)$	$[\eta]_0/V_0 \left( \frac{A_0}{\eta_s} - 1 \right)$
[8]	$2.0 \times 10^6$	3.273	4.398	0.744
	$1.3 \times 10^6$	2.092	2.156	0.970
	$8.0 \times 10^5$	1.602	1.701	0.942
	$3.0 \times 10^5$	0.679	0.640	1.061
[6]	$2.2 \times 10^6$	3.400	3.286	1.035
	$1.0 \times 10^6$	1.850	2.019	0.916
	$3.5 \times 10^5$	0.750	0.719	1.043

Table 6  
The values of the parameters obtained, by processing literature data

References	$M_w$	$A_0$ (Pa s)	$\alpha$	$\beta$	$\gamma$	$\eta_{sp}$ meas./ $\eta_{sp}$ calc.
[3]	$7.0 \times 10^6$	14.07	7.80	1025	40	$1.000 \pm 0.075$
	$5.3 \times 10^6$	6.35	7.80	780	10	$1.000 \pm 0.289$
	$2.2 \times 10^6$	4.05	7.80	220	2	$1.000 \pm 0.076$
	$1.0 \times 10^6$	1.81	7.80	110	0	$1.000 \pm 0.038$

#### 4.3. Rheo-thinning fluids: xanthan-based solutions

The viscosity of different molecular weights xanthan solutions at 25 °C was studied by Milas et al. [3] who presented their results in the following form:

$$\log \eta_{sp} = f(C[\eta]_0)$$

If one applies the same methodology as that used for hyaluronan, the values of  $A_0$ ,  $\alpha$ ,  $\beta$  and  $\gamma$  identified from the experimental data reported by Milas et al. [3] for xanthan solutions can be obtained, as summarized in Table 6.

The concentration range is smaller in this case to compare with hyaluronan solution, i.e. from  $6.25 \times 10^{-2}$  to 2 g L<sup>-1</sup> for xanthan with molecular weight of  $7.0 \times 10^6$  and from 0.25 to 2 g L<sup>-1</sup> for the three others xanthans. The values of  $\eta_{sp}$  were found in the range of  $0.3\text{--}6 \times 10^3$ . As in the previous case, one can consider that Eq. (15) fits very well the experimental data under study and that the  $\alpha$  coefficient is molecular weight independent and seems therefore to be characteristics to the chemical structure of the solute. The values of  $A_0$  were also obtained and the deduction of the limit intrinsic viscosity  $[\eta]_0$ , was also made in this case. Table 7 summarizes these data, from which it is worth to note that the values of the limit intrinsic viscosity calculated from  $A_0$  are lower than those given by Milas et al. [3], by 35% for the xanthan of molecular weight of  $5.3 \times 10^6$  and by 15% for the three other xanthans, as shown in Table 7. It is interesting to note that the values of  $A_0$  corresponding to  $M_w$  of  $7 \times 10^6$ , as deduced from the values of  $A$  reported in Table 2, gave a  $[\eta]_0$  of  $11.8 \pm 0.6$  m<sup>3</sup> kg<sup>-1</sup>, which is 12% higher than the values given by Milas et al. [3].

#### 4.4. Rheo-thinning fluids: carboxymethylcellulose-based solutions

The same approach was applied to CMC solutions and the obtained results are summarized in Table 8.

Fig. 3 illustrates the dependence between the values of  $\ln A$  and  $C$ , which allows the evaluation of Eq. (14). One can states

Table 7  
The values of  $A_0$  and that of deduced limit intrinsic viscosity  $[\eta]_0$

Reference	$M_w$	$[\eta]_0$ L/g from literature	$[\eta]_0 = V_0 \left( \frac{A_0}{\eta_s} - 1 \right)$	$[\eta]_0/V_0 \left( \frac{A_0}{\eta_s} - 1 \right)$
[3]	$7.0 \times 10^6$	10.50	8.865	1.184
	$5.3 \times 10^6$	6.15	4.001	1.357
	$2.2 \times 10^6$	2.90	2.549	1.138
	$1.0 \times 10^6$	1.34	1.140	1.175



Table 8  
The values of the parameters obtained, by processing literature data

Polysaccharides	$A_0$ (Pa s)	$\alpha$	$\beta$	$\gamma$	$\eta_{sp}$ meas./ $\eta_{sp}$ calc.
CMC A	3.37	12.5	60	1.3	$1.00 \pm 0.48$
CMC B	1.035	8.8	20	0.9	$1.00 \pm 0.22$

that the CMC studied by Ciceron [16] and Sabiri [11] is very close to CMC A and that investigated by Yamanaka [1] has an intermediate behaviour between CMC A and CMC B.

In conclusion, it can be established that, regardless the chemical structure of the solute, its viscosity in the Newtonian regime can be presented by the following expression:

$$A = A_0 \exp\{\alpha[1 - \exp(-\beta\varphi)]\exp(\gamma\varphi)\} \quad (16)$$

which for the lowest values of  $\varphi$ , tends to the following limit form:

$$\begin{aligned} \frac{A}{A_0} &= \exp \alpha\beta\varphi \\ &= 1 + \alpha\beta\varphi + \frac{1}{2}(\alpha\beta\varphi)^2 + \frac{1}{6}(\alpha\beta\varphi)^3 + \dots \end{aligned} \quad (16a)$$

or

$$\frac{A}{A_0} = \frac{\eta_{sp} + \varphi}{C[\eta]_0 + \varphi} \cong \frac{\eta_{sp}}{C[\eta]_0}$$

and

$$\varphi = \frac{C[\eta]_0}{\frac{A_0}{\eta_s} - 1} \cong \frac{\eta_s}{A_0} C[\eta]_0$$

This formalism leads to a relationship similar to that established by Kwei et al. [26] for the same conditions. In fact, if one replaces in the Eq. (16),  $A/A_0$  and  $\varphi$  by their expression as a function of  $C[\eta]_0$ , it follows:

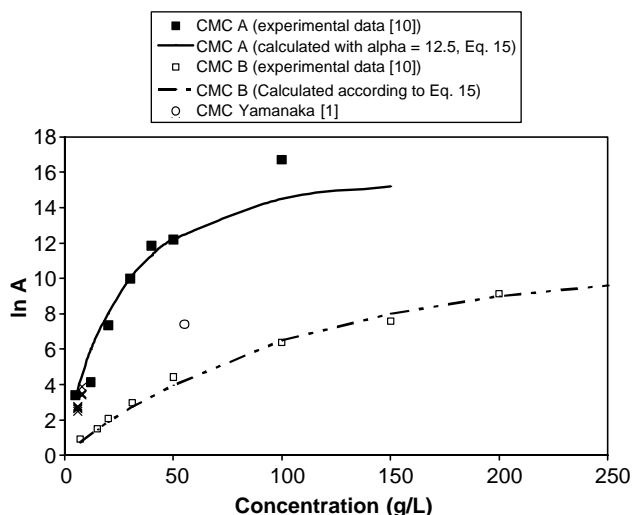


Fig. 3.  $\ln A$  versus concentration plot of the solute for the CMC studied here.

$$\begin{aligned} \frac{\eta_{sp}}{C[\eta]_0} &\cong 1 + \alpha\beta \frac{\eta_s}{A_0} C[\eta]_0 + \frac{1}{2} \left\{ \alpha\beta \frac{\eta_s}{A_0} C[\eta]_0 \right\}^2 \\ &+ \frac{1}{6} \left\{ \alpha\beta \frac{\eta_s}{A_0} C[\eta]_0 \right\}^3 + \dots \end{aligned}$$

and thus

$$\frac{\eta_{sp}}{C[\eta]_0} \cong 1 + kC[\eta]_0 + \frac{1}{2}\{kC[\eta]_0\}^2 + \frac{1}{6}\{kC[\eta]_0\}^3 + \dots \quad (17)$$

where

$$k = \frac{\alpha\beta}{\frac{A_0}{\eta_s} - 1} \quad (18)$$

## 5. Relations between the different parameters of Eq. (16)

Table 9 reports the most relevant data related to this review. Different remarks could be drawn from these data:

- The first one concerns the average values of  $k$ , which is about 0.4 ( $0.38 \pm 0.19$ ), i.e. the same value as that of Huggins constant reported by Kwei et al. [26].
- The second important remark is related to the values of  $\alpha$  which seem to be molecular weight independent.
- Then, the values of  $A_0$ ,  $\beta$  and  $\gamma$ , which increased with the values of the molecular weight.
- The  $\alpha$  coefficient seems to depend only on the molecular structure of the polysaccharide. That is why it was decided to take into account these values for the expressions relating  $\beta$  and  $\gamma$  to  $A_0$  and  $A_0$  to  $M$ .

In order to simplify the deduced equation, it was decided to use the following dimensionless numbers  $A_0/\eta_s$  which is the ratio between the limit of the hypothetical viscosity of the solute and the viscosity of the solvent (aqueous solvent), and  $MV_0/(18 \times 10^{-3})$ , which is the ratio between the limit molar volume of the solute and that of the solvent (aqueous solvent).

Fig. 4 represents the plot of  $\log[\alpha^2(A_0/\eta_s)]$ , as a function of  $\log[\alpha^2(MV_0/18 \times 10^{-3})]$ .

This figure evidences that there is a linear dependence between these entities and leads to the following equation:

$$\alpha^2 \frac{A_0}{\eta_s} = \left[ \alpha^2 \frac{MV_0}{18 \times 10^{-3}} \right]^{0.823 \pm 0.020} \quad (19)$$

Eq. (19) is a very close to that established by Mark–Houwink:

$$[\eta]_0 = NM^a$$

Eq. (19) has two main advantages, namely: (i) it deals with dimensionless parameters, and (ii) its validity was checked for a wide range of molecular weights, i.e. from  $10^2$  to  $10^7$  g mol<sup>-1</sup>. Eq. (19) was applied to CMC A and CMC B solutions to deduce their apparent molecular weights, which were found to be  $1.7 \times 10^6$  and  $3.5 \times 10^5$ , respectively.

Fig. 5 represents the plot of  $\log(\alpha\beta)$ , as a function of  $\log[\alpha^2 A_0/\eta_s]$ .

Table 9  
The values of  $A_0$ ,  $\alpha$ ,  $\beta$  and  $\gamma$ , as well as that of the deduced  $k$

Product	$\eta_s$ (Pa s)	$V_0$ (m <sup>3</sup> kg <sup>-1</sup> )	$M_w$ (g mol <sup>-1</sup> )	$A_0$ (Pa s)	$\alpha$	$\beta$	$\gamma$	$K$
Glycerol	$1.005 \times 10^{-3}$	$7.66 \times 10^{-4}$	92.1	$4.44 \times 10^{-3}$	0.38	3.840	2.742	0.427
Hyaluronan	$9.84 \times 10^{-4}$	$6.2 \times 10^{-4}$	$2.0 \times 10^6$	6.980	8.50	240	9.0	0.288
	$9.84 \times 10^{-4}$	$6.2 \times 10^{-4}$	$1.3 \times 10^6$	3.422	8.50	143	5.6	0.350
	$9.84 \times 10^{-4}$	$6.2 \times 10^{-4}$	$8.0 \times 10^5$	2.700	8.50	97	4.4	0.300
	$9.84 \times 10^{-4}$	$6.2 \times 10^{-4}$	$3.0 \times 10^5$	1.015	8.50	38.5	0.5	0.317
	$9.84 \times 10^{-4}$	$6.2 \times 10^{-4}$	$2.2 \times 10^6$	5.215	8.50	206	10	0.330
	$9.84 \times 10^{-4}$	$6.2 \times 10^{-4}$	$1.0 \times 10^6$	3.205	8.50	110	5	0.287
	$9.84 \times 10^{-4}$	$6.2 \times 10^{-4}$	$3.5 \times 10^5$	1.141	8.50	37	1	0.271
	$9.84 \times 10^{-4}$	$6.2 \times 10^{-4}$	$7.0 \times 10^6$	14.07	7.80	1025	40	0.559
Xanthan	$9.84 \times 10^{-4}$	$6.2 \times 10^{-4}$	$5.3 \times 10^6$	6.350	7.80	780	10	0.943
	$9.84 \times 10^{-4}$	$6.2 \times 10^{-4}$	$2.2 \times 10^6$	4.045	7.80	220	2	0.417
	$9.84 \times 10^{-4}$	$6.2 \times 10^{-4}$	$1.0 \times 10^6$	1.810	7.80	110	0	0.466
CMC A	$9.84 \times 10^{-4}$	$6.2 \times 10^{-4}$	–	3.37	12.5	60	1.3	0.219
CMC B	$9.84 \times 10^{-4}$	$6.2 \times 10^{-4}$	–	1.035	8.8	20	0.9	0.167

In this case also, there is a linear dependence between these entities and leading to the following equation:

$$\alpha\beta = (0.33 \pm 0.10) \left[ \frac{A_0}{\eta_s} \right] \quad (20)$$

Finally, Fig. 6 shows the plot of  $\log(\alpha^2\gamma)$ , as a function of  $\log[\alpha^2 A_0/\eta_s]$

In this case also, even if there is a big dispersion of the data processed, a linear dependence between these entities can be established, thus leading to Eq. (21):

$$\alpha^2\gamma = \{(9.1 \pm 4.0)10^{-2}\} \left[ \frac{A_0}{\eta_s} \right] \quad (21)$$

### 6. Conclusions

This theoretical study aimed at collecting different data relative to the viscosity of water-soluble polysaccharides solutions and processing them in such a way to establish

some relationships between their viscosity, molecular weight and solution concentration. It could be concluded that Eq. (8), an extension of Cross' model, can be considered as a useful and quite accurate model relating the viscosity and both the shear rate and the solution concentration. The combination of Eqs. (9) and (11), applied within a large domain of shear stress, yielded an acceptable model which calls upon the  $A$  and  $A'$  values and another adjustable parameter ( $k$ ). The value of parameter  $k$  introduced by Eq. (11) and reflecting the sensitivity of the solution toward the shear stress, obeys to the same dependency with respect to concentration independently from the nature of the solute used. A second useful relationship (Eq. (15)) was also succeeded and concerned the relation between the zero-shear viscosity ( $A$ ) and the concentration of the solutions. Finally, the intrinsic viscosity of the solute (Eq. (7)) was correlated to its molecular weights giving an alternative equation to that of Mark–Houwink, established for different polymers and involving the preliminary determination of two constants ( $N$  and  $a$ ).

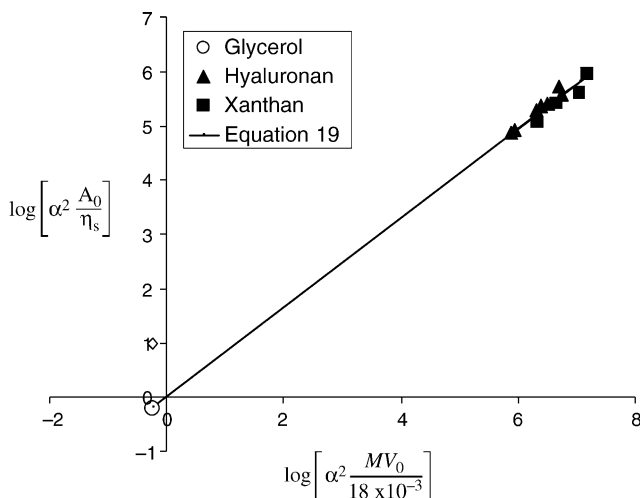


Fig. 4.  $\log[\alpha^2(A_0/\eta_s)]$ , as a function of  $\log[\alpha^2(MV/18 \times 10^{-3})]$  plot, for the polysaccharides studied here.

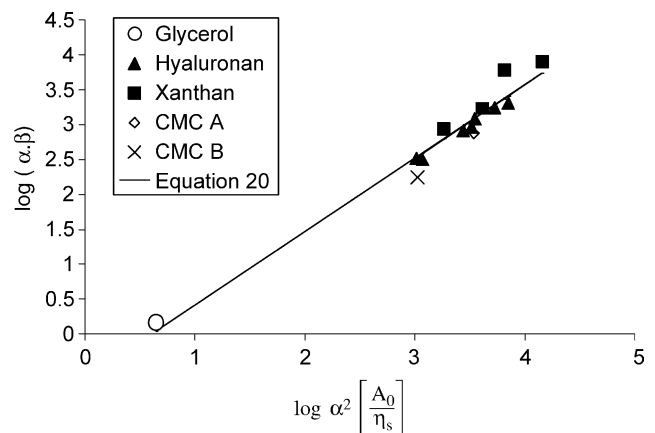


Fig. 5.  $\log(\alpha\beta)$ , versus  $\log[A_0/\eta_s]$  dependence, for the polysaccharides studied here.

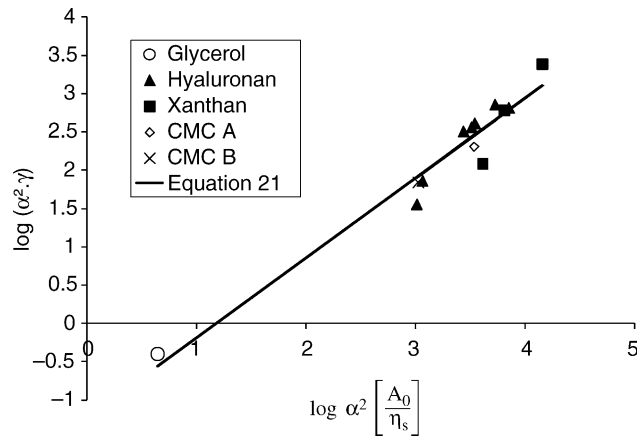


Fig. 6. The plot of  $\log(\alpha^2 \cdot \gamma)$ , as a function of  $\log[A_0/\eta_s]$ , for the polysaccharides studied here.

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