

# The effect of hydrocolloids on the stability and viscosity of cloudy apple juices

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## Abstract

The influence of xanthan gum (XG) and carboxymethylcellulose (CMC) on the colloidal stability of cloudy apple juice has been studied. Concentrations from 0.4–0.5% completely inhibited juice clarification. At lower gum concentrations, juices with CMC were more stable. Z-potential ( $\zeta$ ) was measured by laser doppler electrophoresis. As expected, cloudiness in apple juice increased its stability with  $|\zeta|$  (the more electro-negative, the more stable) following a behavior common to both food gums. Therefore, stability of cloudy juices with food gums could be predicted only in terms of  $\zeta$ . Log–log plot of apparent viscosity ( $\eta_a$ ) vs ( $\dot{\gamma}$ ), showed a typical shear thinning behavior, with a transition from dilute to concentrated solution at some critical concentration. At low shear rates, XG was more viscous than CMC, demonstrating that the greater stabilizing effect of CMC was basically due to its electro-negativity. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords:* Cloudy apple juice; Food gums; Viscosity; Z-potential

## 1. Introduction

Nagel (1992) described a cloudy (opalescent) apple juice as a light, whitish-yellow juice, clearly showing cloudiness, which presents no sedimentation, full-bodied and juicy, but not astringent or bitter. During cloudy juice processing, a small percentage of insoluble particles with a volumetric fraction  $\phi < 0.005$  (Genovese & Lozano, 2000) is retained in suspension, maintaining a light opaque color.

One of the main problems with cloudy apple juice production is the assurance of cloud stability (Beveridge & Harrison, 1986; Gierschner & Baumann, 1988; Genovese, Elustondo, & Lozano, 1997). Even after prolonged storage, none, or only a very small part, of the cloud particles should precipitate. In order to retain more particles or stabilize the juice during more prolonged periods, hydrophilic colloids (hydrocolloids or food gums) have been assayed (Da Silva & Rao, 1992; Da Silva, Gonçalves, & Rao, 1992). Hydrocolloids may be used in food suspensions due to their functional properties: water-holding capacity, regulation of the rheological properties and ionization in aqueous solutions, leading to stabilization of insoluble particles.

In terms of ionization, food gums may or may not have electrical charge. Fruit juices turbidity is caused by particles with a positively charged nucleus of carbohydrates and proteins, surrounded by negatively charged pectins (Yamasaki, Yasui, & Arima, 1964). Partial pectinolysis would carry to positive nucleus exposition, aggregation between polyanions and polycations, and finally flocculation. This clarification could then be avoided by alginates addition (Belitz & Grosch, 1997).

Since juice particles are negatively charged, addition of food gums with negative charge is expected to increase electrostatic repulsive forces between particles. Yamasaki et al. (1964) found that negatively charged colloids (like sodium alginate, CMC and arabic gum) in concentrations as low as 0.05%, completely inhibit apple juice clarification. Furthermore, gum macromolecules adsorption on particles may give rise to steric repulsion.

The objective of this work was to study the influence of two food gums, xanthan gum (XG) and carboxymethylcellulose (CMC) on the stability of cloudy apple juice, in order to better understand the forces involved in this complex colloidal system.

## 2. Material and methods

Cloudy apple juice of 10° Brix was obtained at the

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laboratory by steam-heating the pulp during crushing (thereby inhibiting enzymatic browning and juice clarification) and pressing the mash through a filter, with the equipment and procedures previously described (Genovese et al., 1997). Keltrol-HP xanthan gum (XG) (Monsanto Co., Merseyside, UK) and sodium carboxymethylcellulose (CMC) (MW = 771,000) were from Fluka (New-Ulm., Switzerland). Gums dosage was in the range 0–0.5%. Gums (solid basis) were added to cloudy juices and vigorously agitated in a magnetic stirrer for 1.5 h at room temperature, achieving complete dissolution. Soluble solids at 20°C were determined according to Association of Official Analytical Chemists (1980) method number 932.12.

### 2.1. Determination of apparent viscosity

A Bohlin model CVO Rheometer (Bohlin Reologi UK Ltd., UK) was used to measure shear stress ( $\tau$ ) vs shear rate ( $\dot{\gamma}$ ). A concentric cylinder (diameter = 2.5 cm) geometry was employed. The gap between cylinders (1.25 mm) was enough to ensure no obstruction due to juice particles (<5  $\mu\text{m}$ ). The tests were conducted at 25°C.

### 2.2. Opacity determinations

Opacity was determined with a Hunterlab Ultrascan XE spectrophotometer (Hunter Assoc. Laboratory, Reston, VA, USA) in the reflectance mode. Opacity is defined as the ratio between the CIE Y parameter determined in a 1 cm path cuvette, both against white and black background, respectively:

$$Op = 100(\text{CIE } Y^{\text{white}}/\text{CIE } Y^{\text{black}}) \quad (1)$$

It was found (Genovese et al., 1997) that stable turbidity in cloudy apple juice can be obtained after 15 min centrifugation at  $4200 \times g$  (room temperature). The ratio between the opacity after ( $OP_a$ ) and before ( $OP_b$ ) centrifugation was defined as stable turbidity (ST%):

$$ST\% = 100(OP_a/OP_b) \quad (2)$$

Opacity was measured immediately after the process of gum dilution.

### 2.3. Measurement of z-potential ( $\zeta$ )

The stability of a colloidal system is determined by the sum of the electrical double layer repulsive and van der Waals attractive forces, which the particles experience as they approach one another. For colloidal stability, the repulsive forces must be dominant. There are two fundamental mechanisms that affect dispersion stability: (i) steric repulsion, that involves polymers added to the system adsorbing onto the particle surface and causing repulsion; and (ii) electrostatic (charge) repulsion that is the effect on particle interaction due to the distribution of charged species in the system.

Z-potential measurements are used to assess the stability

of colloidal systems as it is a very good index of the magnitude of the interaction between colloidal particles. The magnitude of the z-potential gives an indication of the potential stability of the colloidal system. In general, when all the particles have a large negative or positive z-potential, they will repel each other and there is dispersion stability. On the other hand, when the particles have low z-potential values then there is no force to prevent the particles coming together. The dividing line between stable and unstable dispersions is generally taken at either +30 or –30 mV. Particles with z-potentials which are more positive or more negative than +30 mV and –30 mV respectively, are normally considered stable (Sherman, 1970). The z-potential is not the potential actually on the particle surface, but the potential measured by electrophoresis, in which the particle is moved by an external electric field. Under these conditions, the particle moves together with the ions in the Stern layer, and it is the potential just outside this bound layer (also called the hydrodynamic or shear plane) which determines the speed of movement. Z-potential is lower than the potential at the particle surface. Z-potential changes with salt concentration, potential determining ion concentration (pH) and steric effect of surfactants and macromolecules.

In this work,  $\zeta$  was measured by laser doppler electrophoresis with a Malvern Zetasizer 3000 (Malvern Instrument Inc., London, UK) using a He–Ne laser at 633 nm and the technique called optical heterodyning. The formula used depends on the relative sizes of the particle and its double layer. Colloid chemists refer to the value of  $ka$ , where  $k$  is the Debye–Huckel constant and  $a$  is the particle radius. In the case of cloudy apple juice, where the particle is big and the double layer is thin, then  $ka \gg 1$  and the  $\zeta$  is given by the Smoluchowski equation:

$$\zeta = \frac{\eta u}{\epsilon} \quad (3)$$

where  $\eta$  is the viscosity of the medium,  $\epsilon$  is the dielectric constant and  $u$  is the particle mobility. The instrument uses Eq. (3) to analyze the data. Samples were diluted 1:10 prior to determination. The results given below are the average values of five replicas for each experimental condition.

## 3. Results and discussion

### 3.1. Z-potential results

Fig. 1 shows the effect of gum content on ST%. As expected, cloud stability increased with hydrocolloid, reaching  $ST\% \cong 100$  (full stability) at 0.4% XG content. This maximum colloid stability value was reached with only 0.3% CMC. Fig. 2 shows the variation of  $\zeta$  with gum content. It can be observed that  $\zeta$  potential reduced when adding CMC and XG, being more electronegative with CMC up to 0.3%. This result is in accordance with the values reported in Fig. 1. Z-potential determination for xanthan gum at concentrations higher than

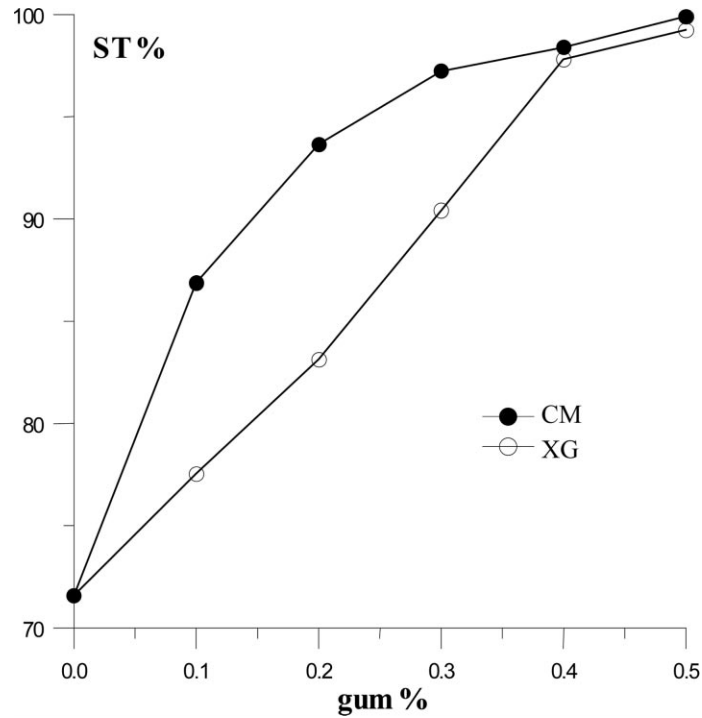


Fig. 1. Stable turbidity [ST%, defined in Eq. (2)], as a function of the food gum content (CMC = carboxymethylcellulose; XG = xanthan gum).

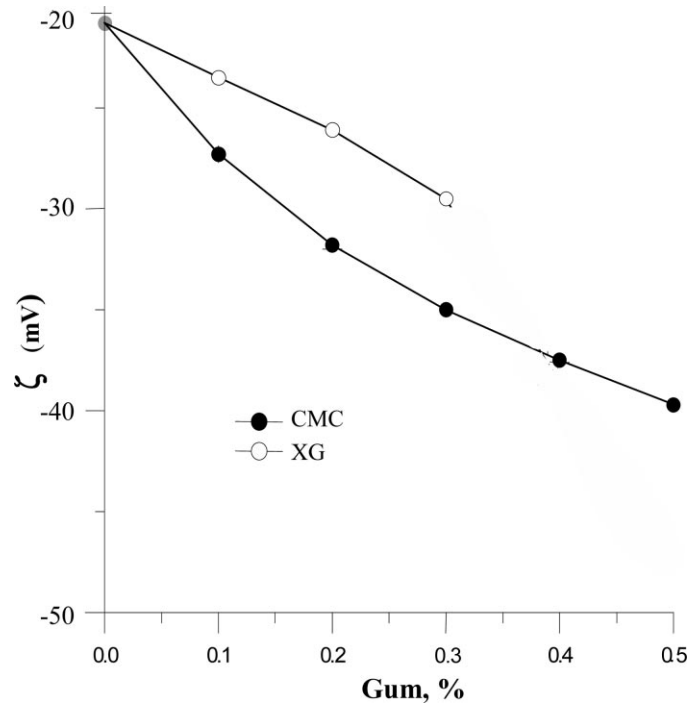


Fig. 2. Z-potential ( $\zeta$ ) in cloudy apple juice as a function of the food gum content (CMC = carboxymethylcellulose; XG = xanthan gum).

0.3% showed serious difficulties attributable to a gel structure development and was not plotted. When ST% was plotted as a function of  $\zeta$  (Fig. 3) a very well defined behavior was observed, independently of the type and concentration of hydrocolloid added.

### 3.2. Viscosity results

Apparent viscosity was calculated as  $\eta_a = \tau/\dot{\gamma}$ . It was observed that for diluted gum solutions, reduction in viscosity with increasing shear rate is relatively minor. This

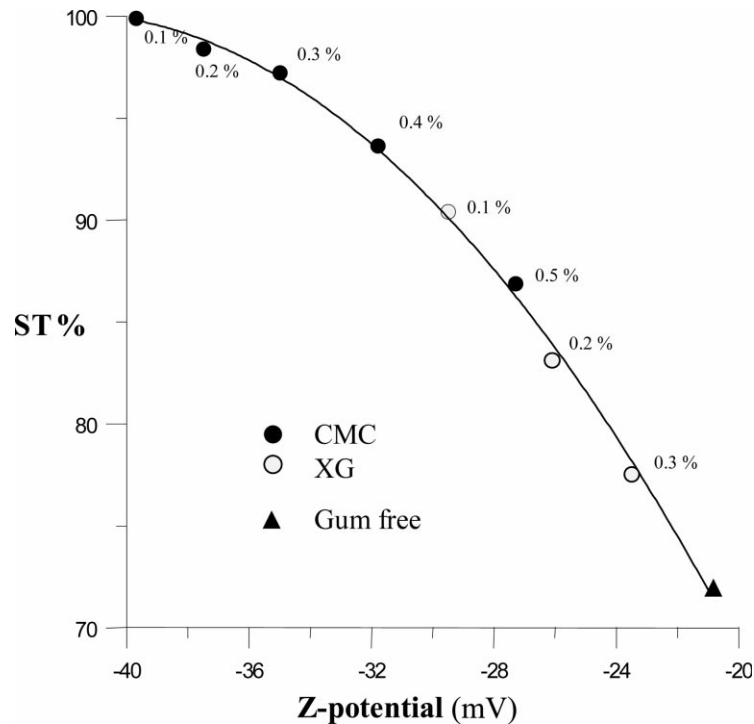


Fig. 3. Stable turbidity (ST%) in cloudy apple juice with added gums, as a function of Z-potential ( $\zeta$ ) (CMC = carboxymethylcellulose; XG = xanthan gum).

behavior was attributed to the alignment of transiently elongated coils in the direction of flow during shear (Morris, Cutler, Ross-Murphy, & Rees, 1981). However, for concentrated solutions, the behavior is quite different because macromolecules coils form an 'entangled' network structure (Graessley, 1974). There is a continuous replacement of macromolecules in the network at low  $\dot{\gamma}$  values, and no change in viscosity occurs. By increasing the rate of shear the number of cross-linked macromolecules decreases and viscosity is reduced. On the other hand, as concentration increases, the movement of macromolecules is restricted and non-Newtonian behavior appears at lower shear rates.

Fig. 4 shows a log–log plot of  $\eta_a$  vs  $\dot{\gamma}$ , with type and concentration of hydrocolloid as parameters. The Newtonian plateau described by Graessley (1974) was observed for both gums (XG and CMC). It was also detected that, at low shear rate, cloudy juices with XG showed higher viscosity than the same juice with CMC. This behavior was mainly attributed to the lower molecular weight of CMC (Bagley, 1992), both gums having practically the same degree of ramification. When XG was added, juices lost their Newtonian behavior at lower  $\dot{\gamma}$ . This behavior, attributed to the formation and breaking of hydrogen bonds, was also noted in galactomannan and polyacrilamide solutions (Kulicke & Porter, 1980). By increasing  $\dot{\gamma}$ , the apparent viscosity of cloudy juice with CMC or XG is similar, at the same gum concentration. The non-Newtonian range depends not only on the molecular weight, but on weight distribution and type and extension of polymer branching (Bagley, 1992). Finally, juices with added XG are

highly pseudoplastic at elevated  $\dot{\gamma}$  values, due to the destruction of intermolecular associations (Da Silva et al., 1992).

### 3.3. Intrinsic viscosity

The hydrodynamic volume of polymers in general and food gums in particular, can be characterized through their limit viscosity number, or intrinsic viscosity:

$$[\eta] = \lim_{c \rightarrow 0} \left( \frac{\eta_r - 1}{c} \right) \quad (4)$$

where  $c$  is the polymer concentration and  $\eta_r$  is the relative viscosity. Calculation of  $\eta_r$  and  $[\eta]$  requires the zero shear rate viscosity of the polymer solution ( $\eta_0$ ) obtained by modified Cross [Eq. (5)] and Carreau [Eq. (6)] models (Da Silva et al., 1992):

$$\eta_a = \eta_0 / (1 + \alpha \dot{\gamma}^m) \quad (5)$$

$$\eta_a = \eta_0 / [1 + (\lambda_C \dot{\gamma})^2]^N \quad (6)$$

In general, the modified Cross model provided a better fit in the case of CMC solutions. The Carreau equation fitted viscosity behavior well when XG was added to cloudy apple juice (Abdel-Khalik, Hassager & Bird, 1974). Obtained values of  $\eta_0$  for CMC and XG, as well as constants  $\alpha$ ,  $m$  [Eq.(5)],  $\lambda_C$  and  $N$  [Eq. (6)] are listed in Tables 1 and 2, respectively.

The viscous force which opposes particles sedimentation could be considered proportional to  $\eta_0$ , since it occurs

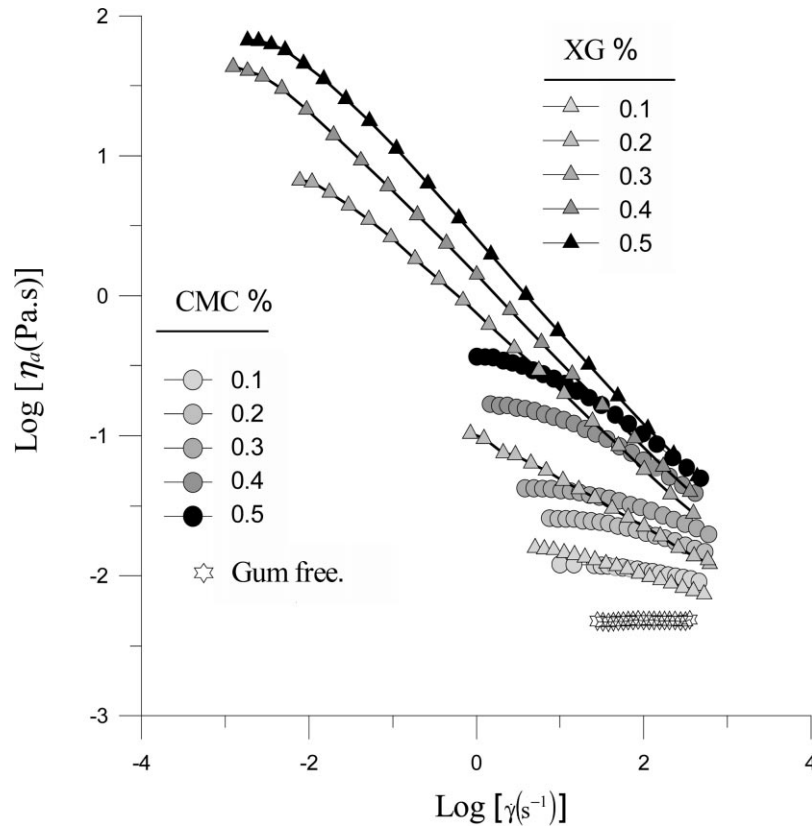


Fig. 4. A log–log plot of  $\eta_a$  vs  $\dot{\gamma}$  in cloudy apple juice, with type and concentration of food gum as parameters.

at very low shear rates. Considering these  $\eta_0$  values are greater for XG, the major stabilizing effect of CMC should be mainly due to its greater electro-negativity, which leads to mayor particle repulsion and avoids agglomeration.

Table 1  
Fitted parameters of Eq. (5) valid for carboxymethylcellulose (CMC). Values in parentheses are standard errors;  $\eta_0$ , zero shear rate viscosity of the polymer solution;  $\alpha$ , time constant, related to the relaxation time of the polymer solution; m, dimensionless exponent

CMC, % (w/w)	$\eta_0$ (Pa.s) $\times 10^2$	$\alpha$ (s <sup>m</sup> ) $\times 10^2$	M	$r^2$
0.1	1.273 (0.035)*	1.039 (0.132)	0.600 (0.004)	0.9922
0.2	2.843 (0.062)	2.844 (0.631)	0.559 (0.035)	0.9963
0.3	4.705 (0.277)	4.454 (0.894)	0.541 (0.017)	0.9981
0.4	19.99 (0.0340)	1.351 (0.352)	0.580 (0.020)	0.9989
0.5	46.50 (6.11)	2.278 (0.734)	0.596 (0.026)	0.9991

Table 2  
Fitted parameters of Eq. (6) valid for xanthan gum (XG). Values in parentheses are standard errors;  $\eta_0$ , zero shear rate viscosity of the polymer solution;  $\lambda_c$ , time constant, related to the relaxation time of the polymer solution; N, dimensionless exponent

XG, % (w/w)	$\eta_0$ , (Pa.s) $\times 10^2$	$\lambda_c$ (s)	N	$r^2$
0.1	1.619 (0.005)	0.120 (0.004)	0.0945 (0.0004)	0.9995
0.2	13.20 (2.130)	2.176 (0.495)	0.1633 (0.0095)	0.9978
0.3	732.2 (73.20)	79.12 (6.00)	0.2587 (0.0382)	0.9995
0.4	4,570 (302)	375.4 (53.40)	0.2909 (0.0186)	0.9999
0.5	7,044 (283)	201.4 (24.50)	0.2977 (0.0056)	0.9998

The two equations employed for determining  $[\eta]$  are (Da Silva et al., 1992):

$$\eta_{sp}/c = [\eta] + k_1[\eta]^2c \tag{7}$$

$$(\ln \eta_r)/c = [\eta] + k_2[\eta]^2c \tag{8}$$

where  $\eta_{sp} = (\eta_r - 1)$  is the specific viscosity; and  $k_1$  and  $k_2$  are Huggins and Kraemer constants, respectively, which are theoretically related by the equation  $k_1 + k_2 = 0.5$ . Calculated intrinsic viscosity resulted  $[\eta] = 10.44$ , with  $k_1 = 0.5996$  and  $k_2 = -0.0996$ , for cloudy juice with added CMC. This result is in accordance with that obtained by Castelain, Lefebvre, and Doublier (1986). On the contrary, values obtained with XG were not reliable, probably due to gel formation.

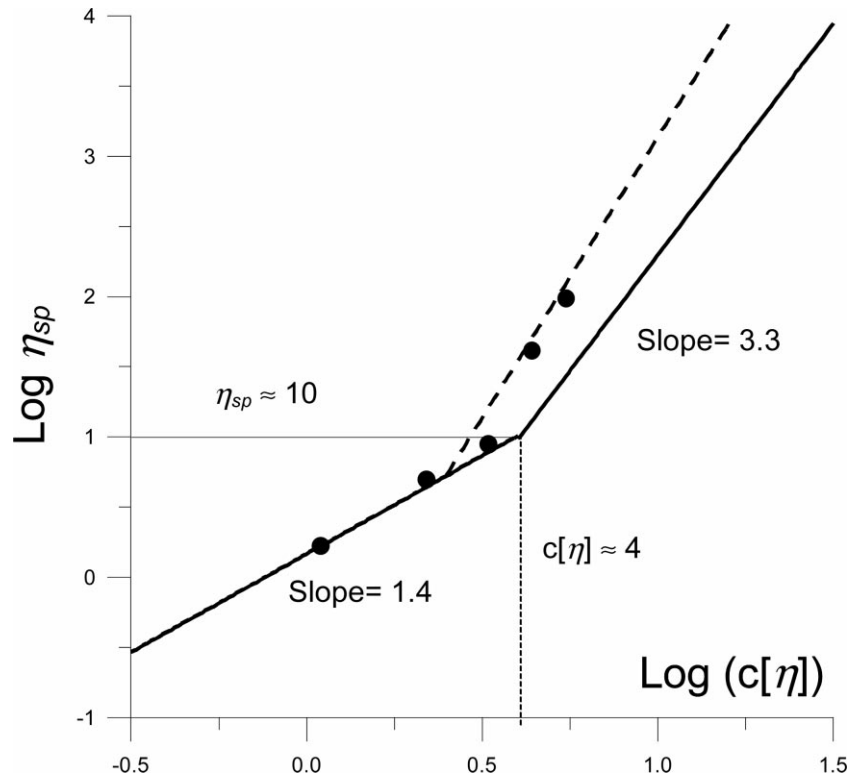


Fig. 5. Variation in the  $\eta_0$  value of food gums with 'coil overlap parameter'. Solid line represents Morris et al. (1981) generalized results. Dotted line represents galactomannan and hyaluronate aqueous solutions deviation (Morris et al., 1980).

### 3.4. Critical concentration

Morris et al. (1981) found that a transition from dilute to concentrated solution behavior occurs at a critical concentration,  $c^*$ , which marks the onset of coil overlap and inter-penetration. A useful parameter which describes the degree of occupancy of a random coil polymer solution is the 'coil overlap parameter'  $c[\eta]$ . Log–log plotting of  $(\eta_{sp})$  vs  $c[\eta]$  was found to behave in the same way as most polysaccharides (Morris et al., 1981), represented as a solid line in Fig. 5. Two regions are very well defined: (i) a region of dilute dispersions with slope = 1.4; and (ii) a region of concentrated dispersions where the viscosity dependence on concentration follows a 3.3 power. A transition occurs at  $c[\eta] \cong 4$ . However, some deviation from the general behavior was found in both galactomannan (Doublier & Launay, 1981) and hyaluronate (Morris, Rees, & Welsh, 1980) aqueous solutions. This deviation, which is more in agreement with the results obtained in this work, is also plotted in Fig. 5 (dotted line). Such divergence was attributed to specific intermolecular associations between regular and rigid chain sequences in addition to the simple process of interpenetration.

Morris et al. (1981) also showed that independently of the

food gum employed, log–log plots of  $(\eta/\eta_0)$  against  $(\dot{\gamma}/\dot{\gamma}_{0.1})$ , where  $\dot{\gamma}_{0.1}$  is the rate of shear at which  $\eta = 0.1 \eta_0$ , are practically identical for all concentrate solutions. Eqs. (5) and (6) and data list in Tables 1 and 2 were used to calculate  $\dot{\gamma}_{0.1}$  from the known  $\eta_0$  values. Fig. 6 shows a typical Morris plot for the two food gums employed. Only low concentration XG solutions exhibit some deviation from the model proposed by Morris et al. (1981). This deviation was attributable to the method of estimation of  $\eta_0$  by extrapolation.

### 4. Conclusions

Results show that, adding 0.4–0.5% by weight of CMC or XG to a non-centrifuged cloudy apple juice, turbidity was stable for extended periods of storage. Although CMC shows a lower  $\eta_0$  than XG at low shear rates, the first is more effective for stabilizing cloudiness when added to a natural cloudy apple juice. This higher stabilizing power of CMC is attributed to its higher electro-negativity, which increases the particle to particle repulsion. Therefore, independent of type and concentration of the food gum used,  $z$ -potential may be sufficient to predict the haze stability in cloudy fruit juices.

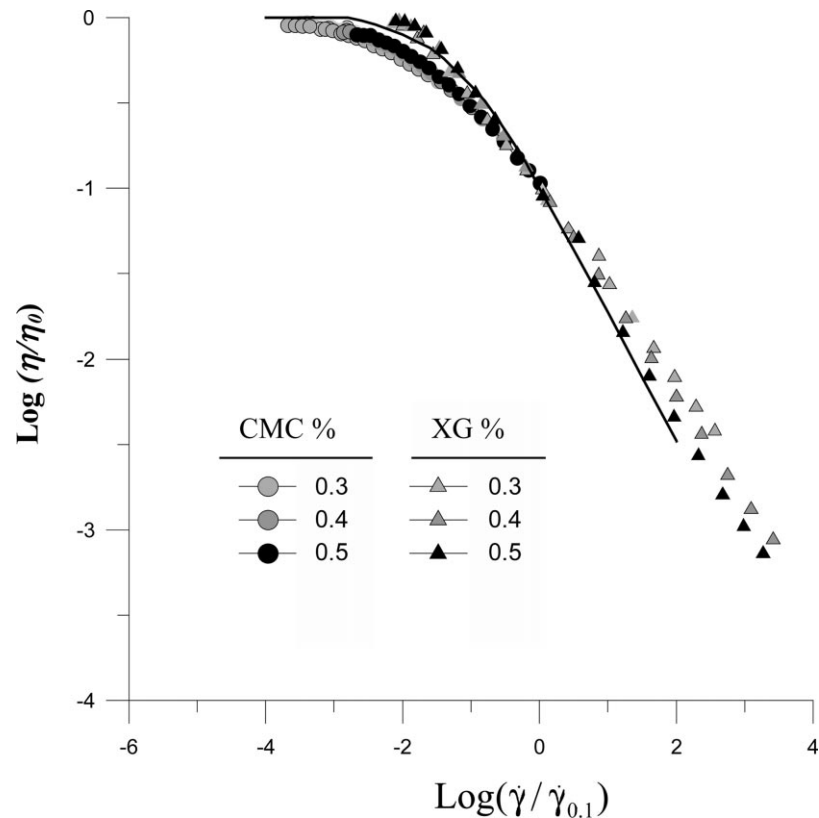


Fig. 6. Morris et al. (1981) type log–log plot of  $(\eta/\eta_0)$  against  $(\dot{\gamma}/\dot{\gamma}_{0.1})$ , with type and concentration of food gum in cloudy apple juice as parameters. Solid line represents generalized Morris et al. (1981) results.

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