

Short communication

Estimation of viscosity of highly viscous fermentation media containing one or more solutes

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Abstract

Viscosity and density data are collected at different temperatures for aqueous solutions of glucose, carboxymethyl cellulose (CMC), or both the solutes and used to check the form of a predictive model proposed in this study for viscosity estimation of mixtures of non-electrolyte solutes in Newtonian fermentation broths. The model, which derives from the well-known Guzman–Andrade equation and is based on the Eyring theory, supposes a separate contribution of each solute to total viscosity, which linearly increases with solute concentration and exponentially decreases with temperature. Percentage deviations between theoretical and experimental viscosity values of both, the binary and ternary mixtures, are usually <5%, thus confirming the validity of the present approach. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The negative influence of viscosity on the oxygen transfer rate in non-Newtonian fermentation systems forming highly viscous products, like xanthan gum, is well documented [1–4]. This effect, which is recognized as the major cause of specific productivity decrease in aerobic bioprocesses, may be the result of a substrate diffusivity reduction in the extracellular polymer layer around the cell [5] and can be minimized by reducing the consequent resistance of the mass transfer by a high shear stress [1]. Unfortunately, however, strong aeration and agitation cause foaming [6], loss of volatile metabolites [7,8], and cell damage [9], thus often provoking reductions in both, the productivity and cell growth. An interesting alternative to minimize these effects, consisting in decreasing viscosity of plant cell cultures by increasing osmotic pressure, has recently been proposed [10].

Very little is known on the physical phenomena taking place in highly viscous (viscoelastic) media [11]. Narayanan et al. [12] suggested that the small bubbles would coalesce with large, free-rising bubbles and reduce substrate transfer coefficient in highly viscous liquids. In these non-New-

tonian systems, broth viscosity is shear-rate dependent and, thus, any viscosity correlation must include shear rate to be meaningful.

On the other hand, a remarkable effect of viscosity on the productivity has recently been evidenced also in Newtonian systems like those used for starch hydrolysate alcohol fermentation. It has been demonstrated that, contrary to processes forming highly viscous products, the addition in a common culture medium of significant amounts of viscosity-raising additives, such as carboxymethyl cellulose (CMC), up to given thresholds of viscosity and temperature may result in significant productivity rise [14–17]. In the light of the results recently presented and discussed by our group on the effects of both, the temperature and CMC concentration on glucose diffusivity [13], this very strange observation could only be justified by supposing a decrease in substrate (glucose) diffusivity due to the polymer layer around the cell, greater than that of the product (ethanol), which could bring about a reduction of product inhibition.

The foregoing remarkable productivity rise provides an example of the importance of studies that are nowadays addressed to a better understanding of these phenomena, among which are those devoted to the viscosity prediction in Newtonian fermentation broths and to the estimation of products as well as substrates diffusivities [18], those dealing with the influence of the operating conditions on both

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viscosity [19] and diffusivity [20], and, finally, those aiming at determining the influence of viscosity on product distribution of chemical reactions [21,22].

The experimental viscosity data of aqueous glucose and/or CMC solutions are used in this work to check a general model, based on the approximate theory developed by Eyring et al. [23,24], which can usefully be employed to predict viscosity of Newtonian fermentation systems, with no necessity of considering any influence of shear rate. To this purpose, the influence of temperature on viscosity as well as the additive contribution of each solute are taken into consideration.

2. Theory

We consider here a way to express the viscosity of dilute solution of one or more solid solutes in a liquid, such as water. We can start by assuming that the viscosity of a solution (μ) can be expressed as the viscosity of the pure liquid solvent (μ_o) plus a contribution of the solute. In the first approximation, we can assume that the solute contribution is simply proportional to its concentration (C_i). That is to say:

$$\mu = \mu_o + C_i k_i \quad (1)$$

If the viscosity and solute concentration are expressed in $\text{g m}^{-1} \text{s}^{-1}$ and g m^{-3} , respectively, the proportionality constant k has the unit of $\text{m}^2 \text{s}^{-1}$. In the presence of more than one solute in the solution, an additive contribution to the total viscosity is given by:

$$\mu = \mu_o + \sum_i C_i k_i \quad (2)$$

We now take into account the effect of temperature: it is well known that the viscosity of a liquid decreases with temperature; an empirical relationship widely used to quantify this behaviour is the Guzman–Andrade equation [23]:

$$\mu_o = A_o \exp\left(\frac{B_o}{T}\right) \quad (3)$$

This equation is very simple and fits with excellent approximation the experimental data for a wide variety of liquids, both inorganic and organic [23]. Our hypothesis here is to utilise a dependence similar to that of the Guzman–Andrade equation to express the temperature influence on the viscosity of solutions on each term of Eq. (2). This leads to:

$$\mu = A_o \exp\left(\frac{B_o}{T}\right) + \sum_i C_i A_i \exp\left(\frac{B_i}{T}\right) \quad (4)$$

In this paper, the viscosity of aqueous solutions simultaneously containing glucose and carboxymethyl cellulose, either separately or together, has been experimentally investigated. We will use the subscripts ‘w’, ‘G’ and ‘CMC’ to

indicate water, glucose and carboxymethyl cellulose, respectively, so that Eqs. (2) and (4) can be written as:

$$\mu = \mu_w + C_G k_G + C_{\text{CMC}} k_{\text{CMC}} \quad (5)$$

and

$$\mu = A_w \exp\left(\frac{B_w}{T}\right) + C_G A_G \exp\left(\frac{B_G}{T}\right) + C_{\text{CMC}} A_{\text{CMC}} \exp\left(\frac{B_{\text{CMC}}}{T}\right) \quad (6)$$

3. Materials and methods

Solutions of glucose, CMC, or both the solutes in water were prepared using all pure-grade reagents and bidistilled water purchased from Carlo Erba, Milan.

The kinematic viscosities of the different solutions were determined by calibrated Ostwald viscosimeters. To this purpose, following the suggestion of Gholap et al. [21] for hydroxymethyl cellulose solutions up to $10 \times 10^3 \text{ g m}^{-3}$, a Newtonian behaviour has been considered for all solutions within the whole experimental domain of CMC and glucose concentrations tested in this study.

The density was determined in glass cylinders by the liquid level displacement provoked by the immersion of calibrated densimeters into the solutions.

The dynamic viscosity has then been estimated as the product of the kinematic viscosity and the relative density.

Both the above-mentioned properties were determined at different temperatures by immersing the viscosimeters or the cylinders of densimeters into the water bath of a Tamson TC45 thermostat connected, according to circumstances, to a Tamson TK20 refrigerator.

4. Results and discussion

4.1. Aqueous solutions of glucose

Fig. 1 shows the dependence of the viscosity of aqueous glucose solutions on glucose concentration ($10 \times 10^3 < C_G < 200 \times 10^3 \text{ g m}^{-3}$) at various temperatures. It is evident from Fig. 1 that, as suggested in this paper, the viscosity of dilute aqueous glucose solutions linearly depends, to a good approximation, on glucose concentration, at least within the glucose concentration range of practical significance in the field of fermentations ($0 < C_G < 300 \times 10^3 \text{ g m}^{-3}$). According to Eq. (1), each straight line starts from a value which should correspond to the viscosity of pure water at a given temperature. The low deviations (<6%) between the μ_w values calculated at different temperatures and those reported in the literature for pure water [24] provide a first indication of the validity of the present approach.

Fig. 2 reports the natural logarithms of μ_w and k_G , the latter estimated by the slopes of the straight lines of Fig. 1,

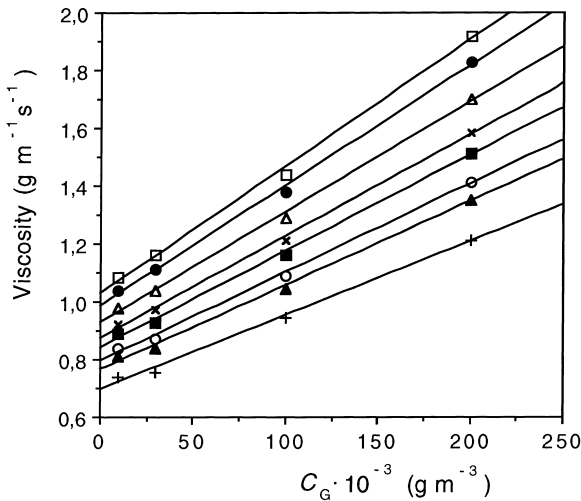


Fig. 1. Viscosity data determined at different temperatures for aqueous solutions of glucose with variable concentration. Temperature (°C): (□) 20; (●) 22; (△) 25; (×) 28; (■) 30; (○) 33; (▲) 35; and (+) 40.

functions of the inverse of the absolute temperature. The excellent straight lines obtained for both these sets of data confirm the validity of the suggested dependence of the above parameters on the temperature, analogous to the Guzman–Andrade equation. A least-square minimization routine, applied to only that part of Eq. (6) concerning glucose, yields the values of the parameters A_w , B_w , A_G and B_G as reported in Table 1. From the literature data of water viscosity collected between 0 and 80°C [24], the following values of the parameters appearing in Eq. (3) can be calculated for water: $A_w = 1.77 \times 10^{-3} \text{ g m}^{-1} \text{ s}^{-1}$ and $B_w = 1864.1 \text{ K}$. Although these values are not exactly coincident with those reported in Table 1, the literature values of the viscosity of water appear to be in good

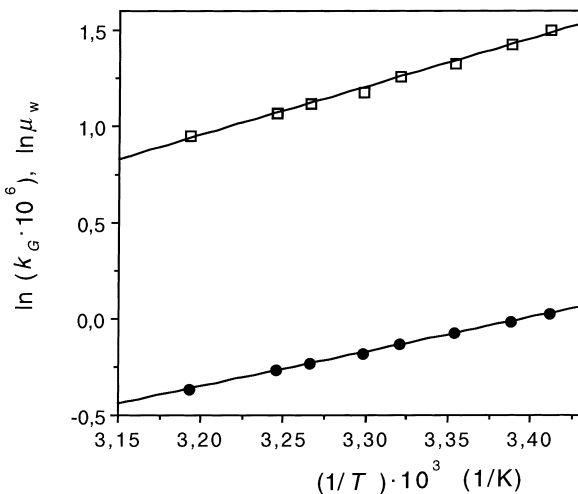


Fig. 2. Temperature dependence of (□) the correlation constant for glucose, k_G , and (●) the viscosity of water, μ_w , extrapolated from glucose solutions at $C_G = 0 \text{ g m}^{-3}$.

Table 1
Values of the parameters appearing in Eq. (6) for water and glucose

	A	B
Water	$2.41 \times 10^{-3} \text{ g m}^{-1} \text{ s}^{-1}$	1774.9 K
Glucose	$8.65 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$	2502.0 K

accordance with the ones estimated in this work, the percentage deviations never exceeding 6% at corresponding temperatures.

4.2. Aqueous solutions of CMC

Analogous results obtained for CMC solutions are shown in Fig. 3. As expected, μ_w decreases with increasing temperature and reaches nearly the same values of viscosity of pure water under conditions of $C_{CMC} = 0 \text{ g m}^{-3}$, which means that the same general Eq. (1) is valid. It should be noticed, from the slopes of the straight lines of this figure, that the values of the correlation constant k_{CMC} are more than three orders of magnitude higher than those of k_G , which is probably due to the very high molecular weight of this efficient viscosity-raising polymer ($M = 350\,000 \text{ g mol}^{-1}$).

As far as the temperature dependence of k_{CMC} is concerned, Fig. 4 evidences a rather similar behaviour as that shown for k_G , which provides a further confirmation of the validity of the Guzman–Andrade equation for aqueous solutions of polar solid solutes. Application of Eq. (6) to CMC provides the values listed in Table 2 for the parameters A_w , B_w , A_{CMC} and B_{CMC} . In this case, the agreement between the values of A_w and B_w estimated from literature data and extrapolated from water CMC solutions is better than that obtained from water glucose solutions.

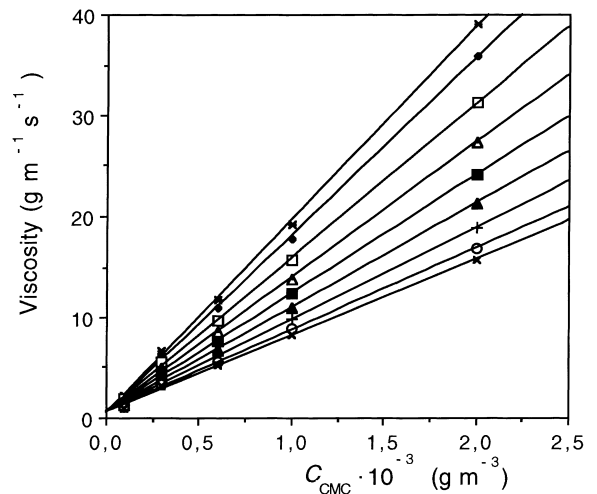


Fig. 3. Viscosity data determined at different temperatures for aqueous CMC solutions with variable concentration. Temperature (°C): (*) 12; (◆) 15; (□) 20; (△) 25; (■) 30; (▲) 35; (+) 40; (○) 45; and (×) 48.

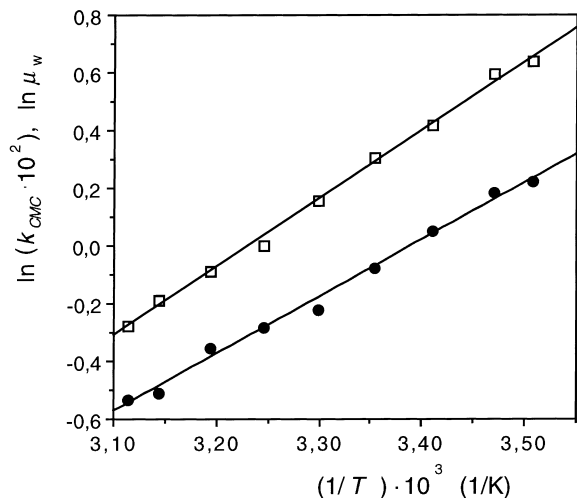


Fig. 4. Temperature dependence of (□) the correlation constant for CMC, k_{CMC} , and (●) the viscosity of water, μ_w , extrapolated from CMC solutions at $C_{CMC} = 0 \text{ g m}^{-3}$.

4.3. Aqueous solutions of CMC and glucose

In this last section, we consider water solutions of both, glucose and CMC. Having already experimentally investigated solutions of one of these solutes independently, we are in the position here to be able to predict the viscosity of these solutions: in Eq. (6) all the parameters are known and we can, therefore, verify if the hypothesis of simple additivity of each solute to the total viscosity is valid. For this purpose, the values of A_w and B_w estimated from the literature data of the viscosity of water have been used.

For a given temperature, the viscosity should vary linearly with any solute concentration. This has been experimentally verified in Fig. 5, where, for $T = 30^\circ\text{C}$, dynamic viscosity has been measured for different values of C_{CMC} and C_G , that have been chosen so that the contribution to total viscosity of each solute is of the same order of magnitude. It will be seen that Fig. 5 depicts a very good agreement between experimental and predicted viscosities.

The effect of the temperature is shown, on the other hand, in Fig. 6, where, for $C_G = 30 \times 10^3 \text{ g m}^{-3}$, the temperature has been changed for various values of C_{CMC} .

Whilst a very good accordance between experimental and theoretical values is evident from Fig. 6, a deeper analysis of the errors would show that the agreement is less satisfactory at low C_{CMC} ($\leq 1.0 \times 10^3 \text{ g m}^{-3}$). This is probably due to the fact that the predicted values of μ are highly sensitive to those of μ_w which, as already stated, have been taken from literature data. It has been shown that Eq. (4)

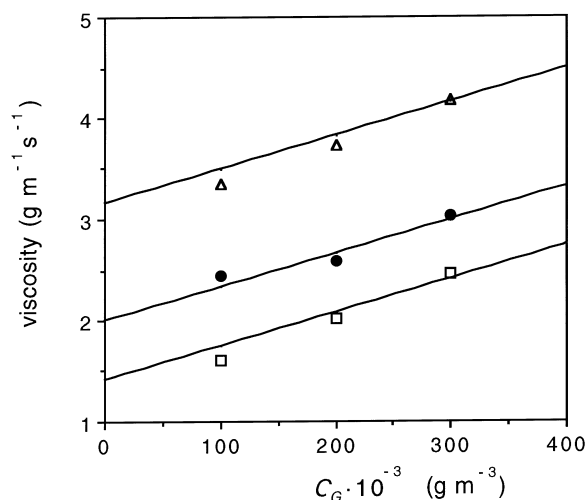


Fig. 5. Dependence at 30°C of viscosity of glucose and CMC solutions on the concentrations of both the solutes. C_{CMC} (g m^{-3}): (□) 50; (●) 100; and (△) 200.

tends to overpredict, even if by only 5%, the viscosity of the pure fluid when its values are extrapolated at solute concentrations approaching zero. Another possible cause of deviation is the relative influence of the experimental error related to the analytical procedure, at least in the presence of this viscosity-raising additive. Both the sources of error, in fact, increase in significance with decrease in the concentrations of both the solutes.

A comparison of the errors estimated in the presence of both, CMC and glucose (Fig. 6), and of glucose alone (Fig. 1), seems to confirm the former hypothesis: viscosity determinations for glucose solutions at variable temperature are characterised by χ^2 values (from 3.99×10^{-4} to 2.18×10^{-3}) about two orders of magnitude lower than

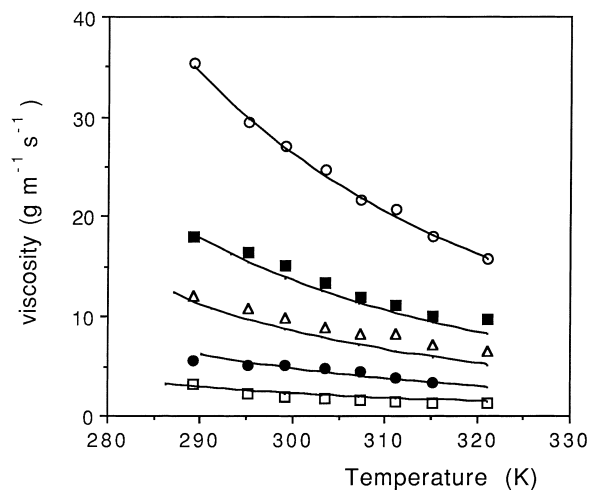


Fig. 6. Comparison between experimental (symbols) and theoretical (curves) viscosity values of aqueous solutions of glucose and CMC at different temperatures. $C_G = 30 \times 10^3 \text{ g m}^{-3}$; $C_{CMC} \times 10^{-3}$ (g m^{-3}): (○) 2.0; (■) 1.0; (△) 0.6; (●) 0.3; and (□) 0.1.

Table 2

Values of the parameters appearing in Eq. (6) for water and CMC

	A	B
Water	$1.62 \times 10^{-3} \text{ g m}^{-1} \text{ s}^{-1}$	1893.6 K
CMC	$5.45 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$	2324.5 K

for solutions containing both the solutes (from 0.133 to 0.377). It is possible that the presence of this high-molecular weight solute induces substantial modifications of the fluid structure that are not observable in the presence of glucose alone.

5. Conclusions

A predictive model based on the additivity of the contribution of solute to the viscosity and on the Guzman–Andrade equation has been proposed and checked with good success in this study by means of viscosity determinations of glucose and CMC solutions at different temperatures.

On account of the general significance of the model, it could likely be used with satisfactory validity for viscosity estimations of solutions containing more than two solutes, at least one of which is highly viscous, also in solvents different from water. For this purpose, additional tests are proposed, using either higher concentrations of CMC (non-Newtonian system) or different solvents and solutes of biological significance in ternary mixtures.

6. Nomenclature

<i>A</i>	pre-exponential factor of Guzman–Andrade equation, Eq. (3) ($\text{g m}^{-1} \text{s}^{-1}$ for water and $\text{m}^2 \text{s}^{-1}$ for glucose and CMC)
<i>B</i>	exponential parameter appearing in Guzman–Andrade equation (K)
<i>C</i>	solute concentration (g m^{-3})
<i>k</i>	correlation constant ($\text{m}^2 \text{s}^{-1}$)
<i>M</i>	molecular weight (g mol^{-1})
<i>T</i>	temperature ($^{\circ}\text{C}$ or K)

Greek letters

μ	dynamic viscosity of the solution ($\text{g m}^{-1} \text{s}^{-1}$)
μ_0	dynamic viscosity of the solvent ($\text{g m}^{-1} \text{s}^{-1}$)
χ^2	chi-square

Subscripts

CMC	carboxymethyl cellulose
G	glucose
<i>i</i>	component <i>i</i>
o	solvent
w	water

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