

Rheology of supersaturated sucrose solutions

M. Quintas ^{a,*}, T.R.S. Brandão ^a, C.L.M. Silva ^a, R.L. Cunha ^{b,1}

^a *Laboratório de Optimização de Processos Alimentares, Escola Superior de Biotecnologia, Universidade Católica Portuguesa, R. Dr. António Bernardino de Almeida, 4200-072 Porto, Portugal*

^b *Laboratório de Engenharia de Processos, Departamento de Engenharia de Alimentos, Faculdade de Engenharia de Alimentos, UNICAMP, Cidade Universitária "Zeferino Vaz", Caixa Postal 6121, CEP 13081-970 Campinas, SP, Brazil*

Keywords: Sucrose solutions; Viscosity; Arrhenius and WLF models; Temperature and concentration effects

Abstract

Sucrose solutions, with concentrations near or superior to saturation, present high potentialities for the candy and pastry industries. Creep measurements under small stresses were done to obtain the rheological properties of highly concentrated sucrose solutions, since such solutions could be in a metastable state and tend to crystallise. The viscosities of these solutions, from 70.0% to 85.2% (w/w), were determined experimentally at different temperatures, from 0 to 90 °C. The temperature dependence of viscosity was studied using experimental and published data for, respectively, high and low concentrations (<70% (w/w)). Results showed that the Arrhenius model describes better the temperature dependence of viscosity for concentrations under saturation and in the high concentration regime the WLF model had a better predicting ability. The effect of concentration on viscosity was observed and included in the Arrhenius and WLF models' parameters. The proposed models were able to successfully describe the data in the corresponding concentration range. These results can be used in predicting the viscosities of syrups for either process design or new products formulation.

Introduction

Sucrose is probably one of the most studied molecules by food scientists, since it plays an important role as an ingredient or preserving agent in many formulations and technological processes. Sucrose solutions, with a concentration near or superior to saturation, present high potentialities for the food industry in areas as different as candies formulation or pastry industry.

In the last years, there was a number of published papers that dealt with the viscosity of concentrated sucrose solutions at temperatures below 20 °C (Bellows & King, 1973; Champion, Hervet, Blond, Le Meste, & Simatos, 1997; Parker & Ring, 1995). However, there is still little informa-

tion available on the rheological properties of such highly concentrated sucrose solutions at usual processing temperatures (room temperature and higher), possibly due to experimental difficulties. These highly concentrated sucrose solutions can be achieved by using high temperatures for short periods of time, followed by fast cooling (Braga da Cruz, MacInnes, Oliveira, & Malcata, 2002; Howell, Ben-Yoseph, Rao, & Hartel, 2002; Izzard, Ablett, & Lillford, 1991). This procedure leads to extremely high viscosity and amorphous solutions with decreased mobility of molecules and thus crystallisation is prevented. The material is in a metastable state and shearing promotes collision between its molecules, leading to nucleation and consequent crystal growth (Hartel, 1993; Shastry & Hartel, 1996). This fact confines the use of steady-state flow measurements to characterise the rheological properties of such solutions. Due to the increasing shear involved in such experiments, crystallisation is faster and there is a change in the rheological behaviour during the measurements.

* Corresponding author. Tel.: +351 22 558 00 58; fax: +351 22 509 03 51.

E-mail address: mafalda@mail.esb.ucp.pt (M. Quintas).

¹ Tel.: +55 19 3788 4047; fax: +55 19 3788 4027.

Nomenclature

a_{Arrh} , b_{Arrh} , c_{Arrh} and d_{Arrh}	parameters of the proposed Global Arrhenius model	R^2	determination coefficient
a_{WLF} , b_{WLF} , c_{WLF} and d_{WLF}	parameters of the proposed Global WLF model	SE	standard error
C	sucrose concentration in weight % (w/w)	SHW	standardised half width (%)
c_1	parameter of the WLF model	t	time (s)
c_2	parameter of the WLF model (°C)	T	temperature (°C or K)
E_a	activation energy (J mol ⁻¹)	T_s	reference temperature (°C or K)
J	creep compliance (Pa ⁻¹)	T_g	glass transition temperature (°C or K)
log	decimal logarithm	V_m	sucrose concentration in molar volume (mol m ⁻³)
MSE	mean square error	η	viscosity (Pa s)
R	universal gas constant (8.314 J mol ⁻¹ K ⁻¹)	η_s	viscosity at reference temperature (Pa s)

Hartel (2001) mentioned this kind of phenomena, when discussing the difficulty of the use of rheological methods in crystallisation studies. Such event is also observed in electro-rheological fluids that change their rheological behaviour due to the required molecular re-orientation caused by the application of an electrical current.

Soesanto and Williams (1981) studied the viscosity of concentrated sugar solutions in the 20–80 °C temperature range using cone and plate rheometry and the falling sphere methods. A mixture of sucrose/fructose (87.5%/12.5% (w/w)) was used, expanding the sugar concentration range without crystallisation. These authors also predicted the behaviour of high concentration sucrose solutions using published data.

Creep test can be used to assess the maximum Newtonian viscosity of a material, if time is sufficiently long to attain viscous flow. In this transient test a small instantaneous stress is applied to the sample, and the response of strain is observed along time. After stress removal, the recovery of strain is also an indication of the rheological behaviour of the material in study (Steffe, 1992). The stress applied to the sample should be rather low, thus minimising the disturbance in the system. This kind of measurements could be interesting for highly concentrated sucrose solutions that are sensitive to shearing.

Sucrose solutions behave as Newtonian fluids (Mathlouthi & Génotelle, 1995) and this behaviour has been reported for concentrations up to 78% (w/w) (Saggin & Coupland, 2004). Due to the small size of sucrose molecules, Newtonian behaviour is expected to uphold at higher concentrations. For this kind of fluid, the creep compliance function (J) shows a linear response with time ($J = 1/\eta \times t$) and no recovery is observed after stress relieve (Steffe, 1992).

This work aimed at: (i) developing an experimental methodology, based on previous existing methods, to study the rheological properties of metastable solutions, (ii) determining the rheological properties of highly concentrated sucrose solutions, and (iii) reviewing the currently used theories of the viscosity dependence on temperature, and its relation with concentration.

Theoretical considerations

The rheological properties of an amorphous material are dependent on molecular mobility (i.e. physical state). The movement of molecules in a system is reflected in its viscosity, which is proportional to the relaxation time of the system. At a temperature, usually named glass transition temperature (T_g), the relaxation time becomes extremely high and T_g is considered as the temperature limit for physical stability of a material (Roos, 1995; Slade & Levine, 1991) and is dependent on both composition and solid content of a material. During the last century, research on the relaxation behaviour of molecules with temperature and concentration has received a lot of interest and several empirical models and theories have been proposed (Peleg, 1992; Roudaut, Simatos, Champion, Contreras-Lopez, & Le Meste, 2004).

An Arrhenius type equation is extensively used in the description of the viscosity dependence on temperature for Newtonian fluids (Barnes, Hutton, & Walters, 1989)

$$\eta = \eta_s \exp \left(-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_s} \right) \right) \quad (1)$$

where η is the viscosity, η_s the viscosity at a reference temperature T_s , E_a the activation energy, T is temperature and R the universal gas constant.

The Arrhenius equation is an empirical model, developed from the theory of the liquid state, based on the movement of molecules through the formation of “holes” in the system (Eyring & Hirschfelder, 1937).

The Arrhenius model has been successfully applied to describe the viscosity temperature dependence of various food products, such as clarified fruit juices (Giner, Ibarz, Garza, & Xhian-Quan, 1996; Ibarz, Gonzalez, & Esplugas, 1994; Ibarz, Pagan, & Miguelsanz, 1992; Vitali & Rao, 1984), vegetable oils in solution (Igwe, 2004) and molasses (Toğrul & Arslan, 2004).

At temperatures near the glass transition, more specifically in the T_g to $T_g + 100$ °C range, experimental data show markedly deviation from the Arrhenius behaviour.

In 1955, Williams, Landel and Ferry (WLF) developed an empirical model to describe the dependence of the viscosity with temperature (Eq. (2)) in the above-mentioned temperature range (Ferry, 1980; Williams, Landel, & Ferry, 1955)

$$\log \eta = \log \eta_s - \frac{c_1(T - T_s)}{c_2 + T - T_s} \quad (2)$$

The constants c_1 and c_2 became “universal”, respectively with the values of 17.44 and 51.6 °C, using T_g as reference temperature.

The WLF model has been used to describe the viscosity temperature dependence of several food materials, mainly at sub ambient temperatures, such as amorphous isomalt (Raudonus, Bernard, Janßen, Kowalczyk, & Carle, 2000), sucrose solutions (Bellows & King, 1973; Champion et al., 1997; Parker & Ring, 1995) and solutions of other low molecular weight carbohydrates, such as glucose, fructose, sorbitol, xylitol (Maltini & Anese, 1995) and trehalose (Miller, Pablo, & Corti, 1997).

The use of the “universal” constants c_1 and c_2 is limited, and the authors themselves cautioned for the indiscriminate use of T_g as reference temperature, since small differences in measured T_g could lead to a deviation in the curve behaviour (Williams et al., 1955). Adam and Gibbs (1965) also questioned the universality of these constants, when developing a molecular-kinetic theory to explain the temperature dependence of relaxation behaviour in glass forming liquids. These authors found a similar expression to the WLF model (Eq. (2)). However, c_1 was dependent on T_s and on the nature of the material itself, and c_2 dependent on both T_s and process temperature (T).

More recently, Peleg (1992) demonstrated that a better prediction of the viscosity is achieved if the reference temperature, used in the WLF model, is within the experimental data range and c_1 and c_2 are model parameters. This approach has been successfully applied in honeys (Sopade et al., 2002).

The molecular movement in a solution is obviously affected by the amount of molecules present and their interaction with water molecules. The effect of concentration on the viscosity is an important factor in food processing, especially in water reducing processes.

The effect of concentration is usually modelled using primary models, which relate viscosity directly with concentration at constant temperature (Ibarz et al., 1992; Rao, Cooley, & Vitali, 1984; Toğrul & Arslan, 2004). Another approach is to include the effect of concentration on the parameters of the previously determined temperature-viscosity model (Simuang, Chiewchan, & Tansakul, 2004; Toğrul & Arslan, 2003). This can be generally done by plotting the Arrhenius or WLF parameters against concentration and finding the best empirical model; usually simple relations, like exponential or power law, describe adequately the data behaviour.

In this work, the Arrhenius and WLF models were applied to both experimental and published viscosity data of sucrose solutions, in a wide range of concentrations.

For low concentrations (from 20% to 60% (w/w) in sucrose), data from published results (Perry & Green, 1998) was used. For concentrations above the saturation level (70–85%), the rheological behaviour was determined experimentally. The choice of the most suitable reference temperature to be used in the WLF model was studied aiming at improving parameters’ estimation (i.e. minimisation of the confidence intervals of the parameters). A study on the concentration dependence of the Arrhenius and WLF models parameters was also conducted.

Materials and methods

Preparation of concentrated sucroses solutions

Solutions with concentrations between 70% and 85% (w/w) were prepared by weighing commercial sucrose and adding distilled water in the desired proportion. The mixture was then heated in a microwave oven (medium power) for short periods (1 min), intercalated with agitation until complete sucrose dissolution (Braga da Cruz et al., 2002).

The use of microwave heating, which results in high temperatures for short time periods, is based on the fact that sucrose in concentrated solutions presents a lag phase in the thermal degradation reaction (Lowary & Richards, 1988) and will not undergo any degradation during solutions preparation. To confirm that no sucrose degradation occurred during the preparation of the solutions, a sample of each solution was analysed in an HPLC system (Quintas, Lobo, Ribeiro, & Silva, 2001).

Water content determination

A Karl Fisher coulometric determination (684 K coulometer, Metrohm, Switzerland) was used to measure the real moisture content for each prepared sucrose concentration. At least three different batches were prepared for each concentration and each batch was analysed three times. The 95% standard error (SE) of the sample water content was calculated.

Rheological measurements

The rheological behaviour of concentrated sucrose solutions was studied at temperatures ranging from 0 to 90 °C, using a rotational controlled stress rheometer (Carrimed CSL² 500, TA Instruments, USA), with stainless steel 6 cm cone and plate geometry.

Preliminary flow experiments were carried out. However, during the measurements there was a molecular re-orientation and consequently nucleation and crystal growth in the metastable samples. A creep experiment was then used in order to avoid the effects of shear increase. Using the same equipment, creep compliance experiments were performed, under a constant stress of 5 Pa, during the necessary time to reach viscous flow. After the stress was withdrawn, the strain was monitored for a period of

time, to observe the recovery. This procedure was repeated in triplicate for each sample. Two true replicates of the experiments were carried out. The viscosity (η) was calculated in each experiment as the reciprocal of the slope of the experimental creep curve observed while stress was applied to the sample.

Data analysis and statistical procedures

The Arrhenius and WLF models (Eqs. (1) and (2), respectively) were fitted to both experimental and published viscosity data in the tested temperature range, for each sucrose concentration. The effect of the WLF model reference temperature on the quality of the regression was analysed. Both studies were performed using the non-linear regression analysis tool from software package STATISTICA[®] 6.0 (StatSoft, Tulsa, OK, USA). The Gauss–Newton algorithm for minimisation of the least squares function was used. The statistical indicators for the quality of the regression, coefficient of determination (R^2) and the mean square error (MSE, i.e. the sum of squares of residuals divided by the corresponding degrees of freedom), and the 95% standard error of the parameters (SE) were obtained directly from the software. A study on the effect of sucrose concentration on the Arrhenius and WLF parameters was also carried out and global models were proposed for both cases. This study was performed using non-linear regression analysis with the simplex algorithm (Nelder & Mead, 1965) for function minimisation, programmed in Fortran 77 language (Fortran 5.1, Microsoft Corporation[®], 1990). The 95% SE of the parameters were calculated, using the variance–covariance matrix. The quality of the regressions was evaluated on the basis of the R^2 and MSE.

Results and discussion

Water content of the concentrated sucrose solutions

The water content of the prepared solutions is presented in Table 1. Since high temperatures are used in these samples preparation, some evaporation occurs, which may explain in some cases the lower values of water content than expected from the “nominal” concentration, i.e. the concentration calculated with the commercial sucrose and water weights used in the solutions’ preparation.

Rheological behaviour of the concentrated sucrose solutions

Preliminary results showed a Newtonian behaviour, with a linear response of strain during the force application, and no recovery when the force was removed (Fig. 1). However, at some critical values of temperature/concentration there was a strong deviation from the Newtonian behaviour. Such deviation was expressed by a non-linear response on the creep curve after a few seconds

Table 1

Water content of the prepared concentrated sucrose solutions (nominal concentration), corresponding standard error (SE) at 95% and sucrose concentration

Nominal sucrose concentration (w/w%)	Water content (w/w%)	95% SE	Sucrose concentration (w/w%)
70.0	30.03	0.28	69.97
75.0	25.30	0.63	74.70
80.0	20.07	0.44	79.93
82.5	17.10	0.43	82.90
85.0	14.79	0.39	85.21

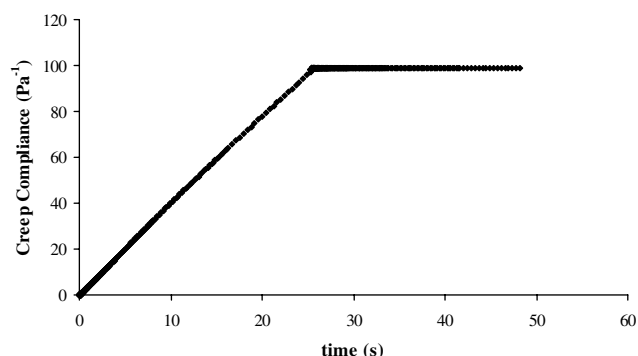


Fig. 1. Typical experimental curve, illustrating a linear response of strain to applied stress, and no recovery after stress removal (results are for an 82.90% sucrose solution at 90 °C).

of linear behaviour. Usually this deviation from linearity of the creep curve is an indication of visco-elastic behaviour. However, after the removal of the stress no recovery was observed, which is typical of Newtonian fluids. This fact suggests that the non-linear response is due to a change in the sample structure. Furthermore, sucrose solutions show Newtonian behaviour in a wide concentration and temperature range and it is not probable that at some critical conditions they behave as visco-elastic materials. These considerations led the authors to believe that molecular re-orientation, and thus crystallisation, was faster at such temperature/concentration conditions. To support this assumption is the fact that this phenomenon occurred in the same concentration/temperature conditions observed by Howell et al. (2002) as the conditions of maximum crystal growth rates. However, no visible crystal growth was observed in our experiments, which may indicate that only nucleation occurred or that the crystals formed were not visible to the naked eye. In these cases, only the first few seconds of the experiment, where Newtonian behaviour was observed, were considered for the viscosity determination. These first seconds represent the moment where the system was disturbed only for a short period and it was assumed that alterations in the samples original structure were minimal. Since a Newtonian fluid presents an instantaneous strain response to stress, these seconds are really representative of the true viscosity of the sample at that

moment. Still, in some concentration/temperature critical conditions, the molecular re-orientation was so fast that the values of viscosity could not be experimentally obtained.

Considering the obtained results and using an ANOVA, no significant difference between the viscosities of replicates was found at 5% significance level and a significant effect of temperature on viscosity was observed. From the experimental results, it could be observed that viscosity of highly concentrated sucrose solutions increased with concentration rise and with decreasing of temperature. The obtained results at each experimental condition are presented in Table 2, with the corresponding standard errors at 95% confidence level.

In order to compare the results, our experimental and published data (Perry & Green, 1998) were evaluated with the Soesanto and Williams (1981) prediction at 20 °C (Fig. 2), using the relationship, based on the Hildebrand free volume theory: $\eta = 6.31 \times 10^{-3} \exp[282(V_m)]$, being V_m sucrose concentration in molar volume. A good prediction for published data (Perry & Green, 1998) can be observed, at low concentrations (20%, 40% and 60% (w/w)). For higher concentrations, determined experimentally, it can be observed an under-prediction by the Soesanto and Williams (1981) expression, which may be due to the free volume limitations near the glass transition.

Moreover, previous results of sucrose solutions viscosity at high concentrations (Reiser, Birch, & Mathlouthi, 1995) are also lower than the values obtained in this work. However, such results were obtained before 1963 using capillary and falling ball viscometers (Christoph, Schmidt, & Senge, 1998). The observed differences could also be attributed to the competing effects of viscosity decrease of the continuous phase and viscosity increase of dispersed phase, due to crystallisation process. Such process occurs in supersaturated solutions, even on quiescent conditions (Howell et al., 2002), indicating that a good alternative to obtain the rheological properties of metastable materials is from transient measurements under low stress or strain.

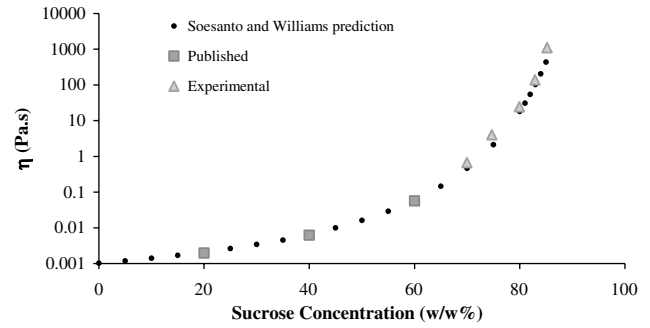


Fig. 2. Comparison of the Soesanto and Williams (1981) prediction of sucrose solutions viscosity at 20 °C with published (Perry & Green, 1998) and experimentally determined data.

Temperature dependence of viscosity

The temperature dependence of viscosity was studied by fitting the Arrhenius and WLF models parameters to experimental and published data. This was because of the deviation in the viscosity behaviour that is observed in the Arrhenius/WLF temperature dependence of viscosity and widely discussed in the literature, which can be a reflex of the change on the molecular interactions and relaxation at higher concentrations.

Arrhenius model

Estimated parameters of the Arrhenius model (Eq. (1)) for the studied concentrations are presented in Table 3. The selected reference temperature was 40 °C, since it has been shown that the use of the middle temperature of the studied range minimises the confidence interval of the Arrhenius parameters (Brandão, 2004; Cohen, Birk, Mannheim, & Saguy, 1994).

It can be observed that the activation energy increases with concentration, which was also observed by other authors in the case of real solutions (Giner et al., 1996; Rao, 1986; Rao et al., 1984; Vitali & Rao, 1984).

The precision of the estimated parameters was evaluated by the standardised half width (SHW%), which is

Table 2
Experimental viscosity (Pa s) of sucrose solutions at different temperatures and concentrations; standard errors (95% confidence level)

T (°C)	Sucrose concentration (w/w%)				
	69.97	74.70	79.93	82.90	85.21
0	$4.70 \pm 9.97 \times 10^{-3}$	$33.68 \pm 1.53 \times 10^{-1}$	641.83 ± 5.08		
10	$1.81 \pm 8.93 \times 10^{-3}$	$11.78 \pm 5.63 \times 10^{-2}$	$99.09 \pm 4.24 \times 10^{-1}$	827.38 ± 5.33	
20	$6.73 \times 10^{-1} \pm 1.41 \times 10^{-3}$	$4.02 \pm 1.07 \times 10^{-2}$	$24.46 \pm 9.71 \times 10^{-2}$	$139.38 \pm 1.46 \times 10^{-1}$	1101.93 ± 15.29
25		$1.58 \pm 3.52 \times 10^{-3}$			
30		$1.58 \pm 5.83 \times 10^{-3}$	$8.40 \pm 8.33 \times 10^{-2}$	$39.37 \pm 3.81 \times 10^{-1}$	180.55 ± 1.75
35					
40	$1.77 \times 10^{-1} \pm 7.60 \times 10^{-4}$	$6.24 \times 10^{-1} \pm 1.84 \times 10^{-3}$		$15.40 \pm 3.26 \times 10^{-1}$	$70.88 \pm 3.90 \times 10^{-1}$
50		$4.34 \times 10^{-1} \pm 5.32 \times 10^{-3}$		$7.19 \pm 6.30 \times 10^{-2}$	$16.57 \pm 2.67 \times 10^{-1}$
60	$1.02 \times 10^{-1} \pm 6.62 \times 10^{-4}$	$2.76 \times 10^{-1} \pm 2.57 \times 10^{-3}$	$1.31 \pm 2.54 \times 10^{-2}$	$3.38 \pm 5.83 \times 10^{-2}$	$8.01 \pm 1.16 \times 10^{-1}$
70		$1.56 \times 10^{-1} \pm 1.04 \times 10^{-3}$	$6.67 \times 10^{-1} \pm 7.42 \times 10^{-3}$	$1.60 \pm 8.06 \times 10^{-3}$	
80	$5.37 \times 10^{-2} \pm 3.53 \times 10^{-4}$			$6.70 \times 10^{-1} \pm 7.34 \times 10^{-3}$	
90		$1.45 \times 10^{-1} \pm 3.42 \times 10^{-4}$	$1.69 \times 10^{-1} \pm 1.13 \times 10^{-3}$	$2.96 \times 10^{-1} \pm 2.19 \times 10^{-3}$	

Table 3

Estimated parameters and corresponding standard errors (95% confidence level) of the Arrhenius and WLF models. Evaluation of the regression quality on the basis of MSE and R^2

Sucrose concentration (w/w) (%)	Arrhenius ($T_s = 40^\circ\text{C}$)			WLF ($T_s = 0^\circ\text{C}$)			$T_s = 0^\circ\text{C}$		
	$\eta_s \pm \text{SE at } 95\%$ (Pa s)	$E_a/R \pm \text{SE at } 95\%$ (K)	MSE	R^2	$\log \eta_s \pm \text{SE at } 95\%$	$c_1 \pm \text{SE at } 95\%$	$c_2 \pm \text{SE at } 95\%$ ($^\circ\text{C}$)	MSE	R^2
20 ^a	$1.22 \times 10^{-3} \pm 3.88 \times 10^{-5}$	$2.37 \times 10^3 \pm 9.34 \times 10^1$	3.75×10^{-9}	0.996	$-2.42 \pm 1.19 \times 10^{-3}$	$2.05 \pm 1.62 \times 10^{-2}$	122.59 ± 1.67	5.87×10^{-7}	1.000
40 ^a	$3.26 \times 10^{-3} \pm 1.47 \times 10^{-4}$	$3.19 \times 10^3 \pm 1.22 \times 10^2$	5.50×10^{-8}	0.997	$-1.83 \pm 1.72 \times 10^{-2}$	$2.95 \pm 2.99 \times 10^{-1}$	141.03 ± 23.16	1.27×10^{-4}	0.999
60 ^a	$2.06 \times 10^{-2} \pm 1.81 \times 10^{-3}$	$4.90 \times 10^3 \pm 3.14 \times 10^2$	6.64×10^{-6}	0.993	$-6.34 \times 10^{-1} \pm 2.44 \times 10^{-2}$	$3.79 \pm 1.35 \times 10^{-1}$	105.51 ± 8.69	5.89×10^{-5}	1.000
69.97 ^b	$1.42 \times 10^{-1} \pm 3.35 \times 10^{-2}$	$7.48 \times 10^3 \pm 5.24 \times 10^2$	2.84×10^{-3}	0.993	$6.98 \times 10^{-1} \pm 1.69 \times 10^{-1}$	3.42 ± 1.01	58.99 ± 39.07	3.18×10^{-3}	0.997
74.70 ^b	$6.40 \times 10^{-1} \pm 1.32 \times 10^{-1}$	$8.47 \times 10^3 \pm 4.56 \times 10^2$	1.47×10^{-1}	0.999	$1.59 \pm 2.21 \times 10^{-1}$	$4.13 \pm 8.98 \times 10^{-1}$	55.79 ± 29.42	1.02×10^{-2}	0.987
79.83 ^b	$8.17 \times 10^{-1} \pm 2.63 \times 10^{-1}$	$1.42 \times 10^4 \pm 6.94 \times 10^2$	13.88	1.000	$2.77 \pm 2.82 \times 10^{-1}$	6.17 ± 1.84	73.01 ± 47.62	1.21×10^{-2}	0.995
82.90 ^b	6.18 ± 1.67	$1.45 \times 10^4 \pm 8.04 \times 10^2$	39.70	1.000	$3.57 \pm 3.88 \times 10^{-1}$	9.13 ± 2.94	115.39 ± 76.82	7.68×10^{-3}	0.995
85.21 ^b	38.07 ± 23.92	$1.54 \times 10^4 \pm 2.92 \times 10^3$	451.45	0.998	5.11 ± 3.69	8.67 ± 8.29	63.41 ± 212.72	9.19×10^{-3}	0.994

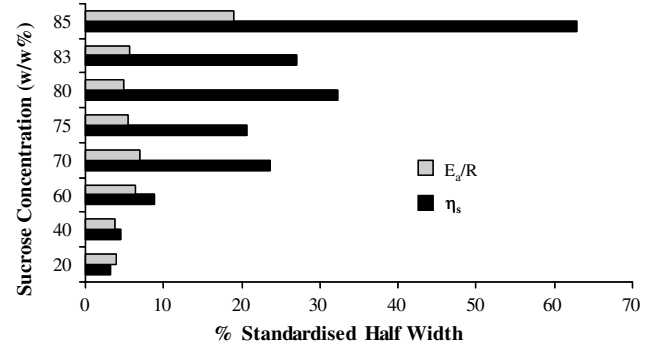
^a Published data (Perry & Green, 1998).^b Experimental data.

Fig. 3. Standardised half width (SHW%) for the estimated Arrhenius parameters as a function of concentration.

calculated dividing the 95% standard error by the value of the estimate. The values obtained are presented in Fig. 3. In all cases the SHW of E_a/R was less than 20%. On the other hand, it can be observed that the SHW of the viscosity at reference temperature (η_s) increases with concentration. The highest value (63%) was observed for 85.21% (w/w) sucrose concentration. The values of R^2 , obtained for each concentration, indicate a good regression procedure, nevertheless the Mean Square Error, MSE, increased with concentration (Table 3). This may indicate that at higher concentrations (lower molecular mobility) a deviation from the Arrhenius behaviour is found, as described in the literature (Adam & Gibbs, 1965; Soesanto & Williams, 1981; Williams et al., 1955).

WLF model

The WLF model (Eq. (2)) was fitted to the available data, using T_g as reference temperature. The referred T_g for sucrose solutions was determined as a function of its composition, by the Gordon–Taylor’s relationship (using $T_{g\text{water}} = -135^\circ\text{C}$ and $T_{g\text{pure sucrose}} = 62^\circ\text{C}$) (Roos, 1995).

The use of T_g as reference temperature conducted, in the majority of the studied cases, to regression convergence problems. Furthermore, in the cases where the regression procedure converged, the results obtained were not significant at 5%. This was not unexpected, since the experimental temperatures are in a larger range than $T_g + 100^\circ\text{C}$.

Hence, a study on the effect of the reference temperature on the quality of the regression was performed. A typical result can be observed in Fig. 4. In most of the cases, both for $\log \eta_s$ and c_1 , a minimum in the SHW (never higher than 30%) was observed when the reference temperature was close to 0°C , which was the lowest temperature used in the experimental determination of viscosity and this is in accordance with Peleg (1992). For c_2 , a minimum of SHW could not be identified, however at 0°C it presented acceptable values, as it can be observed in Fig. 4. The exception to these results was observed at 85.21% (w/w) sucrose concentration, where the SHW both for $\log \eta_s$ and c_1 presented a minimum around 20°C . This observation may be due to the fact that no experimental data could be obtained at temperatures below 20°C , because of the high

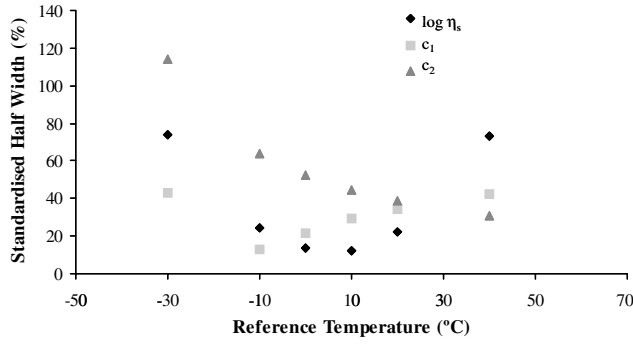


Fig. 4. Typical example of the dependence of the WLF parameters standardised half width (SHW%) with reference temperature (e.g. for 74.70% (w/w) sucrose concentration).

values of viscosity involved at these concentration/temperature conditions. However, it was observed that the MSE was equal (9.19×10^{-3}) when using the values of 0 or 20 °C, as reference temperature. This indicates that, although the precision of the estimates (for 85.21% sucrose concentration) was poorer when using $T_s = 0$ °C, the quality of the regression was acceptable. Based on this analysis, the WLF model was fitted, to both experimental and published data, using 0 °C as the reference temperature (results in Table 3).

The “universality” of the WLF c_1 and c_2 parameters was also studied, by investigating the concentration and reference temperature dependence of these “constants”. It was observed that both c_1 and c_2 are dependent on the reference temperature (Fig. 5), and when the reference temperature is fixed c_1 is dependent on the concentration, whereas c_2 does not present statistically significant concentration dependence (Fig. 6). These findings were in agreement with Adam and Gibbs (1965) conclusions. Results for 85.21% were not included in Fig. 6, due to the above-mentioned estimated precision problems.

Overall it can be concluded, on the basis of the regressions quality, that the Arrhenius model is able to describe better the temperature dependence of viscosity at concentrations below and near saturation (20, 40 and 60%

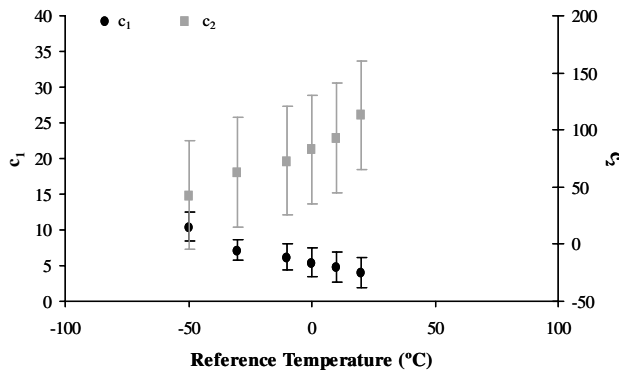


Fig. 5. Typical example of the reference temperature effect on the WLF c_1 and c_2 parameters (e.g. for 79.93% (w/w) sucrose concentration). The bars indicate the 95% confidence interval limits.

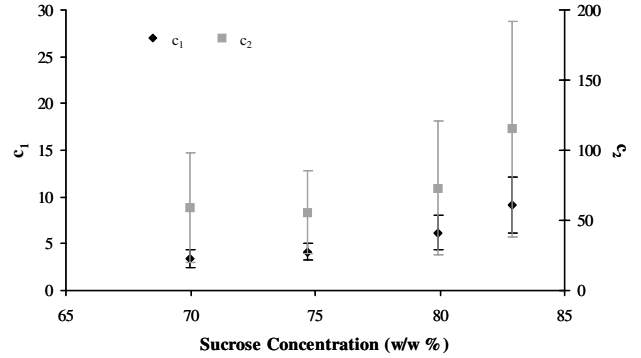


Fig. 6. Concentration dependence of the WLF c_1 and c_2 parameters, using 0 °C as reference temperature. The bars indicate the 95% confidence interval limits.

(w/w) sucrose content). For concentrations above saturation (74.70–85.21% (w/w) sucrose content), the WLF model describes better the temperature dependence of viscosity, when a proper reference temperature is chosen. At 69.97% (w/w) sucrose content, both models were able to describe the temperature dependence of viscosity with similar quality. This can be explained considering that 69.97% is close to the saturation point of sucrose at room temperature (67% (w/w)), and at this concentration the solution is in the transition between a free flowing liquid and a “rubber” type material.

Effect of concentration on the arrhenius and WLF parameters

To describe the viscosity of sucrose solutions in the studied concentration and temperature ranges, the concentration dependence of both the Arrhenius and WLF parameters was modelled.

As a first approach, the previously estimated parameters (Table 3) were plotted against concentration. An exponential relation was found for: (i) E_a/R , in the Arrhenius model and (ii) c_1 and $\log \eta_s$, in the WLF model. Moreover, the reciprocal of the η_s obtained from the Arrhenius model varied linearly with the reciprocal of sucrose concentration.

These relations were embedded in the two models (Eqs (1) and (2)) to describe both temperature and concentration dependence in the low concentration (Global Arrhenius—Eq. (3)) and high concentration (Global WLF—Eq. (4)) regimes

$$\eta = \frac{1}{a_{\text{Arrh}} + b_{\text{Arrh}}/C} \exp \left[c_{\text{Arrh}} \exp(d_{\text{Arrh}}C) \left(\frac{1}{T} - \frac{1}{T_s} \right) \right] \quad (3)$$

where C is the sucrose concentration in weight % (w/w) and a_{Arrh} , b_{Arrh} , c_{Arrh} and d_{Arrh} are parameters determined by non-linear regression analysis

$$\log \eta = a_{\text{WLF}} \exp(b_{\text{WLF}}C) + \frac{c_{\text{WLF}} \exp(d_{\text{WLF}}C)(T - T_s)}{c_2 + (T - T_s)} \quad (4)$$

where a_{WLF} , b_{WLF} , c_{WLF} , d_{WLF} and c_2 are parameters determined by non-linear regression analysis.

Table 4

Estimated parameters and standard errors (95% confidence level) of Global Arrhenius and Global WLF models. Evaluation of the regressions' quality on the basis of MSE and R^2

Global Arrhenius		Global WLF	
a_{Arrh}	$-2.52 \times 10^2 \pm 1.30 \times 10^2$	a_{WLF}	$5.76 \times 10^{-4} \pm 2.14 \times 10^{-6}$
b_{Arrh}	$1.81 \times 10^4 \pm 9.13 \times 10^3$	b_{WLF}	$1.06 \times 10^{-1} \pm 2.79 \times 10^{-4}$
c_{Arrh}	$4.49 \times 10^2 \pm 9.53 \times 10^2$	c_{WLF}	$-1.23 \times 10^{-1} \pm 6.03 \times 10^{-3}$
d_{Arrh}	$4.02 \times 10^{-2} \pm 3.04 \times 10^{-2}$	d_{WLF}	$4.90 \times 10^{-2} \pm 6.93 \times 10^{-4}$
		c_2	69.16 ± 0.11
R^2	0.9995	R^2	0.9837
MSE	2.05×10^{-4}	MSE	2.51×10^{-2}

The parameters of the above models were estimated with the corresponding 95% standard errors, and are presented in Table 4, together with R^2 and MSE for the regressions.

Values of MSE and R^2 reveal a good ability of the proposed models to describe the effects of both temperature and concentration on the viscosity of sucrose solutions. The 95% standard errors determined for the parameters of the Global WLF model (Eq. (4)) are very small, indicating a good estimation procedure. However, this was not found for the Global Arrhenius (Eq. (3)) parameters. This fact is probably due to regression problems with the expression that presents a pre-exponential factor with parameters in the denominator, and consequently it is strongly dependent on the function domain.

Conclusions

Experimental data of viscosity for highly concentrated sucrose solutions were obtained for a wide temperature range and Newtonian behaviour was observed for all the samples. A creep measurement under low stress was used to obtain the rheological properties, since such procedure minimises the disturbance in the system. In respect to the viscosity temperature dependence, it can be concluded that the Arrhenius model was able to describe better data at concentrations below saturation. For higher concentrations, the WLF model had a better ability to describe the temperature dependence of viscosity, if a proper reference temperature is chosen. Such results are in accordance with the glass transition theory. It was also found that the reference temperature affected c_1 and $\log \eta_s$ in the WLF model. Furthermore, the reference temperature that led to better regression results was 0 °C, the lowest experimental temperature used in this study. Models were proposed to describe the simultaneous effects of concentration and temperature on the viscosity, which were based on the Arrhenius and WLF equations, expressing successfully both experimental and published data. The information given by these models can be used in predicting the viscosities of syrups, used in the candy and pastry industries, for either process design or in new products formulation.

Acknowledgements

The present work was supported by CAPES/GRICES—no. 089/02 and POCTI/EQU/49194/02. Author M. Quintas would like to thank Praxis XXI Ph.D. grant BD/20057/99 to Fundação para Ciência e a Tecnologia.

References

- Adam, G., & Gibbs, J. H. (1965). On the temperature dependence of cooperative relaxation properties in glass-forming liquids. *The Journal of Chemical Physics*, 43(1), 139–146.
- Barnes, H. A., Hutton, J. F., & Walters, K. (1989). *An introduction to rheology* (1st ed., pp. 12–14). Amsterdam: Elsevier Science Publishers B.V.
- Bellows, R. J., & King, C. J. (1973). Product collapse during freeze-drying of liquid foods. *AIChE Symposium Series*, 69(132), 33–41.
- Braga da Cruz, I., MacInnes, W. M., Oliveira, J. C., & Malcata, F. X. (2002). Supplemented state diagram for sucrose from dynamic mechanical thermal analysis. In H. Levine (Ed.), *Amorphous food and pharmaceutical systems* (pp. 59–70). Cambridge: The Royal Society of Chemistry.
- Brandão, T. R. S. (2004). Application of non-isothermal methods to the estimation of mass transfer parameters: Analysis of the effect of experimental design and data analysis on the precision and accuracy of the estimates—Appendices (pp. D1–D16). Ph.D. Thesis, College of Biotechnology, Catholic University of Portugal, Porto.
- Champion, D., Hervet, H., Blond, G., Le Meste, M., & Simatos, D. (1997). Translational diffusion in sucrose solutions in the vicinity of their glass transition temperature. *Journal of Physical Chemistry B*, 101(50), 10674–10679.
- Christoph, D., Schmidt, T., & Senge, B. (1998). Flow characteristics of pure and technical sucrose solutions in the temperature range of 30 to 130 °C. *Zuckerindustrie*, 123(11), 876–882.
- Cohen, E., Birk, Y., Mannheim, C. H., & Saguy, I. S. (1994). Kinetic parameter-estimation for quality change during continuous thermal-processing of grapefruit juice. *Journal of Food Science*, 59(1), 155–158.
- Eyring, H., & Hirschfelder, J. (1937). The theory of the liquid state. *Journal of Physical Chemistry*, 41(2), 249–257.
- Ferry, J. D. (1980). *Viscoelastic properties of polymers* (3rd ed., pp. 280–289). New York: John Wiley & Sons, Inc.
- Giner, J., Ibarz, A., Garza, S., & Xhian-Quan, S. (1996). Rheology of clarified cherry juices. *Journal of Food Engineering*, 30(1–2), 147–154.
- Hartel, R. W. (1993). Controlling sugar crystallization in food products. *Food Technology*, 47(11), 99–106.
- Hartel, R. W. (2001). *Crystallization in foods* (1st ed., pp. 72–73). Gaithersburg, MD: Aspen Publishers, Inc.
- Howell, T. A., Jr., Ben-Yoseph, E., Rao, C., & Hartel, R. W. (2002). Howell sucrose crystallization kinetics in thin films at elevated

- temperatures and supersaturations. *Crystal Growth and Design*, 2(1), 67–72.
- Ibarz, A., Gonzalez, C., & Esplugas, S. (1994). Rheology of clarified fruit juices. III: Orange juices. *Journal of Food Engineering*, 21(4), 485–494.
- Ibarz, A., Pagan, J., & Miguelsanz, R. (1992). Rheology of clarified fruit juices. II: Blackcurrant juices. *Journal of Food Engineering*, 15(1), 63–73.
- Igwe, I. O. (2004). The effects of temperature on the viscosity of vegetable oils in solution. *Industrial Crops and Products*, 19(2), 185–190.
- Izzard, M. J., Ablett, S., & Lillford, P. J. (1991). Calorimetric study of the glass transition occurring in sucrose solutions. In E. Dickinson (Ed.), *Food polymers, gels and colloids* (pp. 289–309). Cambridge: The Royal Society of Chemistry.
- Lowary, T. L., & Richards, G. N. (1988). Effects of impurities on hydrolysis of sucrose in concentrated aqueous solution. *International Sugar Journal*, 90(1077), 164–167.
- Maltini, E., & Anese, M. (1995). Evaluation of viscosities of amorphous phases in partially frozen systems by WLF kinetics and glass transition temperatures. *Food Research International*, 28(4), 367–372.
- Mathlouthi, M., & Génotelle, J. (1995). Rheological properties of sucrose solutions and suspensions. In M. Mathlouthi & P. Reiser (Eds.), *Sucrose. Properties and applications* (pp. 126–154). London: Blackie Academic & Professional.
- Miller, D. P., Pablo, J. J., & Corti, H. (1997). Thermophysical properties of trehalose and its concentrated aqueous solutions. *Pharmaceutical Research*, 14(5), 578–590.
- Nelder, J. A., & Mead, R. (1965). A simplex method for function minimization. *The Computer Journal*, 7(4), 308–313.
- Parker, R., & Ring, S. G. (1995). A theoretical analysis of diffusion-controlled reactions in frozen solutions. *Cryo-Letters*, 16, 197–208.
- Peleg, M. (1992). On the use of the WLF model in polymers and foods. *Critical Reviews in Food Science and Nutrition*, 32(1), 59–66.
- Perry, R. H., & Green, D. W. (1998). *Perry's chemical engineers' handbook, international editions* (7th ed., pp. 2–324). Sydney: McGraw-Hill.
- Quintas, M., Lobo, L., Ribeiro, L., & Silva, C. L. M. (2001). Kinetics of high temperature degradation of concentrated sucrose solutions. *Poster presented at EUROCAFT 2001, Berlin, Germany*.
- Rao, M. A. (1986). Rheological properties of fluid foods. In M. A. Rao & S. S. H. Rivzi (Eds.), *Engineering properties of foods* (pp. 1–48). New York: Marcel Dekker, Inc.
- Rao, M. A., Cooley, H. J., & Vitali, A. A. (1984). Flow properties of concentrated juices at low temperatures. *Food Technology*, 38(3), 113–119.
- Raudonus, J., Bernard, J., Janßen, H., Kowalczyk, J., & Carle, R. (2000). Effect of oligomeric or polymeric additives on glass transition, viscosity and crystallization of amorphous isomalt. *Food Research International*, 33(1), 41–51.
- Reiser, P., Birch, G. C., & Mathlouthi, M. (1995). Physical properties. In M. Mathlouthi & P. Reiser (Eds.), *Sucrose. Properties and applications* (pp. 186–222). London: Blackie Academic & Professional.
- Roos, Y. H. (1995). *Phase transitions in foods* (1st ed., pp. 26–47). San Diego, CA: Academic Press.
- Roudaut, G., Simatos, D., Champion, D., Contreras-Lopez, E., & Le Meste, M. (2004). Molecular mobility around the glass transition temperature: A mini review. *Innovative Food Science & Emerging Technologies*, 5(2), 127–134.
- Saggin, R., & Coupland, J. N. (2004). Rheology of xanthan/sucrose mixtures at ultrasonic frequencies. *Journal of Food Engineering*, 65(1), 49–53.
- Shastri, A. V., & Hartel, R. W. (1996). Crystallization during drying of thin sucrose films. *Journal of Food Engineering*, 30(1–2), 75–94.
- Simuang, J., Chiewchan, N., & Tansakul, A. (2004). Effects of fat content and temperature on the apparent viscosity of coconut milk. *Journal of Food Engineering*, 64(2), 193–197.
- Slade, L., & Levine, H. (1991). Beyond water activity: Recent advances based on an alternative approach to the assessment of food quality and safety. *Critical Reviews in Food Science and Nutrition*, 30(2–3), 115–360.
- Soesanto, T., & Williams, M. C. (1981). Volumetric interpretation of viscosity for concentrated and dilute sugar solutions. *Journal of Physical Chemistry*, 85(22), 3338–3341.
- Sopade, P. A., Halley, P., Bhandari, B., D'Arcy, B., Doeblner, C., & Caffin, N. (2002). Application of the Williams–Landel–Ferry model to the viscosity–temperature relationship of Australian honeys. *Journal of Food Engineering*, 56(1), 67–75.
- Steffe, J. F. (1992). *Rheological methods in food processing engineering* (1st ed., pp. 173–176). East Lansing, MI: Freeman Press.
- Toğrul, H., & Arslan, N. (2003). Flow properties of sugar beet pulp cellulose and intrinsic viscosity–molecular weight relationship. *Carbohydrate Polymers*, 54(1), 63–71.
- Toğrul, H., & Arslan, N. (2004). Mathematical model for prediction of apparent viscosity of molasses. *Journal of Food Engineering*, 62(3), 281–289.
- Vitali, A. A., & Rao, M. A. (1984). Flow properties of low-pulp concentrated orange juice: Effect of temperature and concentration. *Journal of Food Science*, 49(3), 882–888.
- Williams, M. L., Landel, R. F., & Ferry, J. D. (1955). The temperature dependence of relaxation mechanisms in amorphous polymers and other glass-forming liquids. *Journal of the American Chemical Society*, 77, 3701–3707.