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Viscosity of concentrated sucrose and trehalose aqueous solutions including the supercooled regime

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The viscosity of aqueous solutions of sucrose and trehalose is analyzed over a wide range of concentrations and temperatures covering the normal liquid and supercooled liquid regions, close to the glass transition temperature. These sugar solutions are fragile systems whose viscosity exhibits temperature dependence with a large departure from Arrhenius behavior. A description of the temperature and concentration dependences of the solution viscosity is given in terms of a scaled Arrhenius representation, which adopts the reduced temperature T_g/T as the state variable. A comparison with results obtained from other theoretical or semiempirical equations is also presented. © 2008 American Institute of Physics. [DOI: 10.1063/1.2932114]

Key words: aqueous solutions; fragility; sucrose; supercooled; trehalose; viscosity.

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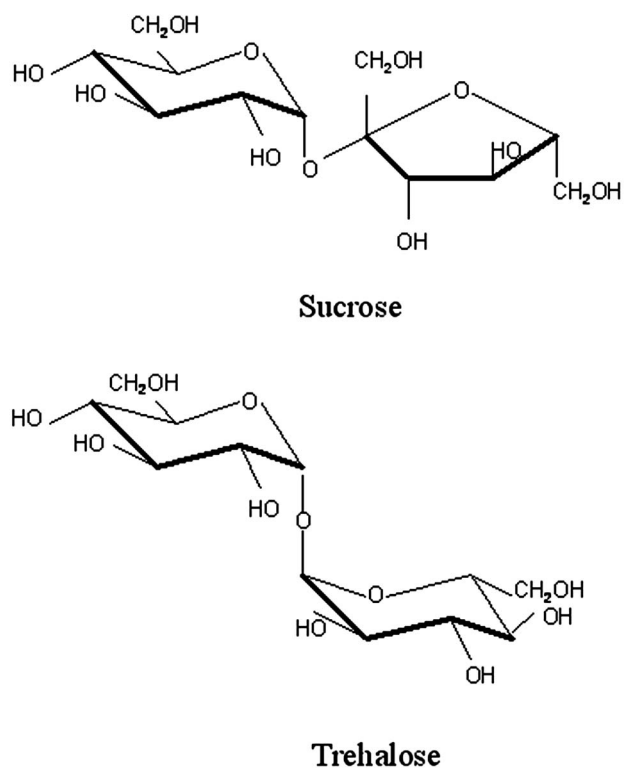


FIG. 1. Chemical structure of sucrose and trehalose (α -D-glucopyranosyl, α -D-glucopyranoside).

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1. Introduction

Sucrose (α -D-glucopyranosyl- β -D-fructofuranose) and trehalose (α -D-glucopyranosyl- α -D-glucopyranoside) are non-reducing disaccharides, whose structures are shown in Fig. 1, widely used as ingredients and preserving agents in the food and pharmaceutical industries and also as cryopreservants to stabilize labile biomolecules in aqueous solutions by a combination of kinetic and specific effects.^{1,2}

Sucrose is one of the most studied sugars, and the viscosity of its aqueous solutions has been measured by several authors for over 100 years. The famous work by Einstein³ on Brownian motion, published in 1906, used sucrose in water to exemplify the validity of the well known equation which relates the solution viscosity to the volume fraction of the

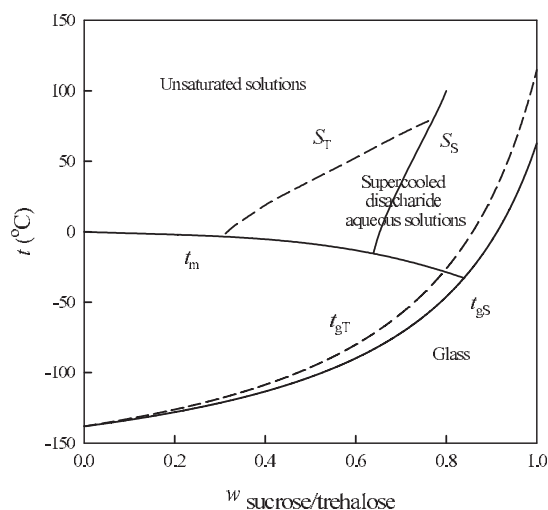


FIG. 2. Supplemented phase diagram for sucrose and trehalose aqueous solutions. t_m corresponds to the equilibrium water melting temperature, S_T and S_S correspond to trehalose and sucrose solubility equilibrium curves, and t_{gT} and t_{gS} correspond to trehalose and sucrose glass transition temperatures.

solute. Since then, many publications have reported viscosity data of aqueous sucrose solutions over a wide range of temperatures and concentrations, being used as standard solutions for viscosity determinations.

On the other hand, trehalose is considered the most effective polyol used as a vitrifying agent in aqueous solution and its cryoprotectant ability has been widely studied in the literature.^{2,4-6}

Considering that water absorption in sucrose and trehalose stabilizing matrices is inevitable during long periods of storage, the study of aqueous disaccharide solutions is of great importance for cryopreservation technology. These sugar-water mixtures are also commonly used in food technology; therefore the analysis of the thermophysical properties of these mixtures is of great interest for this industry. Also, deterioration reactions in these sugar-water systems are determined by the diffusion of reactants in the matrices, which is related to the solution viscosity through the Stokes-Einstein relationship or the corrected Stokes-Einstein equation close to the glass transition temperature.⁷ Therefore, knowledge of the viscosity of aqueous disaccharide solutions in wide concentration and temperature ranges is crucial for the analysis of the validity of the common liquid transport equations as a function of the proximity to the glass transition temperature.

The aim of this work is to perform a comprehensive analysis of all the experimental data available for the viscosity of concentrated sucrose and trehalose aqueous solutions not only in the thermodynamically stable liquid region but also in the supercooled (metastable) region of the supplemented phase diagram of these systems (Fig. 2). This supercooled regime can be reached by increasing the sugar concentration isothermally or by decreasing the temperature at constant concentration.

2. Theoretical Background

2.1. Viscosity Concentration Dependence

The viscosity of aqueous solutions depends on the thermodynamic state parameters solute concentration, temperature, and pressure. From a microscopic point of view, the size and shape of the solute molecules determine the hydrodynamics in a given solvent, as first pointed out by Einstein,³ who related the viscosity of the solution, η , to the volume fraction of the solute in the solution.

Einstein's equation is restricted to dilute solutions and, for this reason, other authors^{8–11} extended his equation in order to take into account the molecular interactions appearing when the concentration of the solute exceeds the infinite-dilution limit. The Jones–Dole equation⁸ is one of the most used expressions in describing the viscosity dependence of solutions with solute concentration.

A suspension model, derived from hydrodynamic considerations, was proposed by Vand¹⁰ and leads to the following expression for the concentration dependence of the viscosity of a solution:

$$\ln \frac{\eta}{\eta_w} = \frac{\nu}{q_0 + q_1 \nu + q_2 \nu^2}, \quad (1)$$

where ν is the solute concentration in g cm^{-3} , η_w is the viscosity of water, q_0 is related to the shape of the molecules and the hydration at infinite dilution, and q_1 and q_2 are related to the hydrodynamic and intermolecular interactions. Using this model, Vand could assign hydration numbers to sucrose in aqueous solutions as a function of temperature, ranging from 10.5 at 0 °C down to 2.5 at 100 °C.

Génotelle¹² used the following equation, proposed by Kaganov,¹³ to describe the viscosity of aqueous sucrose solutions at concentrations up to 85 wt % in the temperature range of 20–80 °C:

$$\ln \frac{\eta}{\eta_w} = A + Bc, \quad (2)$$

where A and B are constants and c is the molar concentration.

All these equations were used to describe the viscosity of sucrose solutions at constant temperature with the resulting fitting parameters being very sensitive to temperature.

2.2. Viscosity Temperature Dependence

The viscosity temperature dependence of some liquids (called “strong” by Angell¹⁴) is well represented by the Arrhenius equation, which linearly relates $\ln \eta$ with T^{-1} (with T the absolute temperature).

On the other hand, the viscosity temperature dependence of some other systems, such as sucrose and trehalose aqueous solutions, deviates from the Arrhenius equation. These liquids were called “fragile” by Angell¹⁴ and exhibit a “super-Arrhenius” temperature dependence of the viscosity

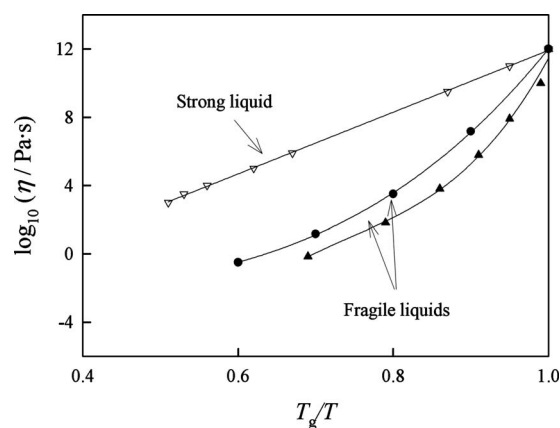


FIG. 3. Viscosity temperature dependence of strong and fragile liquids: (∇) SiO_2 , (\bullet) glycerol, and (\blacktriangle) sucrose at 64 wt %.

or the structural relaxation time in Angell's plot ($\log_{10} \eta$ vs T_g/T), as shown in Fig. 3, with T and T_g expressed in kelvins.

The fragility of a liquid is measured by the viscosity deviation from Arrhenius behavior in the glass transition and is defined by the following equation:

$$m = \left[\frac{\partial \log_{10} \eta}{\partial (T_g/T)} \right]_{T_g}, \quad (3)$$

where T_g is the glass transition temperature of the liquid, that is, the temperature at which the viscosity reaches 10^{12} Pa s or, equivalently, the structural relaxation time τ becomes 100 s, which comes from the consideration that η is proportional to τ , with the proportionality constant the shear modulus.

The temperature dependence of the viscosity of these liquids is usually represented by the well-known Vogel–Tammann–Fulcher (VTF) equation¹⁵

$$\eta = \eta^0 \exp\left(\frac{DT_0}{T - T_0}\right), \quad (4)$$

where η^0 , D , and T_0 are constants. The parameter D decreases with increasing curvature of the Arrhenius plot and is related to the fragility through the relation¹⁵

$$m = 17 + \frac{590}{D}, \quad (5)$$

valid if the preexponent of the conventional Arrhenius activation energy is constrained to 10^{-5} Pa s.

The Williams–Landel–Ferry (WLF) equation,¹⁶ developed to describe the viscosity of polymers in the range between T_g and $T_g + 100$ K, is given by

$$\log_{10} \left(\frac{\eta}{\eta_g} \right) = - \frac{C_1(T - T_g)}{C_2 + (T - T_g)}, \quad (6)$$

where C_1 and C_2 are constants and η_g is the viscosity at T_g . This equation was used for the first time by Soesanto and Williams¹⁷ to describe the viscosity temperature dependence of aqueous sucrose/fructose blends. The WLF equation is

mathematically equivalent to the VTF equation, but the divergence temperatures, T_0 and T_g , do not have the same physical significance.

Rössler^{18,19} analyzed the viscosity of supercooled simple organic liquids and observed two distinct regimes. Close to the glass transition temperature, for viscosities higher than 10–100 Pa s, the viscosity temperature dependence was well described by the WLF equation, while for lower viscosity values, the power-law equation

$$\eta = \eta_0(T - T_c)^\gamma, \quad (7)$$

where η_0 , γ , and T_c are constants, gives a better description of the viscosity temperature dependence. The temperature T_c , which differentiates the two regimes, was found to be related to the glass transition temperature by $T_c/T_g \approx 1.18$ for all the liquids studied and is related to the crossover temperature of the mode-coupling theory developed by Götze and Sjögren,²⁰ which also predicts the power law for the structural relaxation of supercooled liquids.

Other equations for the temperature dependence of viscosity in liquids were derived from the random-walk model. Thus, Richert and Bässler²¹ proposed the following equation:

$$\eta = \eta_0 \exp\left(\frac{T_0}{T}\right)^2, \quad (8)$$

where η_0 and T_0 are constants, for the temperature range $T_g < T < T_c$, whereas the power-law equation could account for the viscosity behavior at temperatures above T_c .

Arkhipov and Bässler reanalyzed the temperature behavior of the viscosity in strong and fragile supercooled liquids and developed a model^{22,23} valid for both types. For fragile liquids, their expressions are

$$\eta = \eta_0 \left[\frac{\pi}{2(\alpha - 1)} \right]^{1/2} \alpha^{(2\alpha - 3)/2(\alpha - 1)} \Gamma(\alpha - 1)^{-1} \left(\frac{T_0}{T} \right)^{(2 - \alpha)/2(\alpha - 1)} \times \exp \left[(\alpha - 1) \left(\frac{T_0}{\alpha T} \right)^{\alpha/(\alpha - 1)} \right] \quad (9)$$

for $T < T_c$ and

$$\eta = \eta_0 2^{(2\alpha - 1)/2(\alpha - 1)} \alpha^{-1} \Gamma(\alpha - 1) \left(\frac{T_0}{T} \right) \times \exp \left[(\alpha - 1) (1 - 2^{-1/(\alpha - 1)}) \left(\frac{T_0}{\alpha T} \right)^{\alpha/(\alpha - 1)} \right] \quad (10)$$

for $T > T_c$, where η_0 and T_0 are constants, Γ is the gamma function, and α is a shape parameter of energy distribution. There is a close relationship between the parameter α and the fragility. Thus, $\alpha \rightarrow 2$ for strong glass-forming liquids, while $\alpha \rightarrow 1$ for fragile glass-forming liquids.

As noted in the previous section, for aqueous solutions, the equations summarized previously are valid for fixed compositions, that is, the parameters of all the equations depend on the solute concentration.

2.3. More General Equations: Concentration and Temperature Dependences

In spite of the importance of an overall description of the concentration and temperature dependences of the viscosity of aqueous solutions (or mixtures in general), there have been few reported efforts to develop empirical or theoretical based equations for the description of the c and T dependences of the viscosity of these systems beyond the infinite-dilution limit.

In the particular case of sugar solutions, Wagnerowski²⁴ represented the viscosity of concentrated aqueous sucrose solutions with the following equation:

$$\log_{10} \frac{\eta}{\eta^*} = x \left(\frac{a}{t + b} - c \right) - d, \quad (11)$$

where x is the sucrose mole fraction, t is the temperature in °C, and η^* is a standard viscosity that makes the logarithm dimensionless, with $a=4120$, $b=91$, $c=11.75$, and $d=2.10$.

Génotelle¹² used a similar empirical equation, which includes the mole fraction of the sugar, x , a reduced temperature, $\Phi = (30 - t)/(91 + t)$, and four constants, namely,

$$\log_{10} \frac{\eta}{\eta^*} = a_1 + a_2 x + \Phi(b_1 + b_2 x^n). \quad (12)$$

Mathlouthi and Génotelle²⁵ used this equation to fit the experimental viscosity data available in 1978 and claimed that it had accuracy better than 1%. However, differences as large as 18% were found between experimental data and the values calculated by the authors (Table 6.3, p. 137, Ref. 25).

Erszterle²⁶ used the free-volume theory for the interpretation of the viscosity of pure sucrose solutions and, more recently, Först *et al.*²⁷ extended Vand's equation (1) to deal with the temperature dependence of the viscosity of aqueous sucrose solutions. These authors assumed that the temperature dependence of q_0 follows an Arrhenius law and derived the following expression for the viscosity:

$$\ln \frac{\eta}{\eta_w} = \frac{v^*}{1 + q_1 v^*}, \quad (13)$$

where $v^* = v q_0^{*-1} \exp(E_a/RT)$ and $q_0^* = q_0 \exp(E_a/RT)$. It was observed that this equation described quite well the viscosity of sucrose solutions in the range of 20–80 °C with $q_0^* = 1.12 \text{ g cm}^{-3}$, $q_1 = -0.248$, and $E_a = 2.61 \text{ kJ mol}^{-1}$.

3. Data Sources

In this section, we will briefly review the sources of viscosity data for concentrated sucrose and trehalose aqueous solutions. The term “concentrated” is arbitrary, but it is used in this work for sugar solutions with concentrations higher than 10 wt %.

3.1. Aqueous Sucrose

The first accurate viscosity measurements of pure aqueous sucrose solutions were performed in 1917 by Bingham and

Jackson²⁸ between 0 and 95 °C on solutions containing 20, 40, and 60 wt % sucrose by using a capillary viscometer. They reported tables with original measured data and interpolated and extrapolated values in the temperature range of 0–100 °C.

Bennett and Nees²⁹ measured the viscosity of sucrose solutions in the temperature interval of 25–70 °C for solutions containing between 66.6 and 76.2 wt % sucrose by using a falling-sphere viscometer. The direct measurements were not reported, but they tabulated interpolated and extrapolated data between 65 and 76 wt % at intervals of 1%.

Landt^{30,31} measured the viscosity of aqueous sucrose between 20 and 90 °C for concentrated solutions (60–80 wt %) by using a Hoeppler viscometer with an uncertainty of $\pm 0.5\%$. He also performed a comprehensive review of all data published up to 1936 and concluded that the viscosity values that he had obtained were several percent smaller than those reported by Bingham and Jackson.²⁸ Jones and Stauffer³² performed very precise viscosity measurements of 20 and 40 wt % aqueous sucrose solutions at 25 °C with an Ostwald viscometer.

The observation by Landt³¹ of discrepancies in the viscosity of concentrated sucrose solutions led Swindells *et al.* to measure the viscosity of sucrose solutions at 30, 40, 50, 60, 65, 70, and 75 wt % over the temperature range of 0–35 °C by using a capillary viscometer similar to that described by Bingham and Jackson.²⁸ These measurements are the basis of Circular 440 of the National Bureau of Standards (NBS).³³ We believe that they measured the viscosity at temperature intervals of 5 °C, as reported in Table 132 (p. 673),³³ while the recommended data for viscometer calibration (Table 130, p. 671), reported between 15 and 25 °C at intervals of 1 °C, were obtained by interpolation. In Circular 440, they also reported viscosity data between 40 and 80 °C in the concentration range of 20–75 wt % at intervals of 1 wt % sucrose based on the data by Bingham and Jackson, Landt, and Bennett and Nees. The authors recalculated the data reported by Landt using higher values for the constants of Landt's viscometer, but they did not describe the equations used to interpolate and extrapolate the results over the range of temperatures and concentrations published.

Two reviews on the viscosity of aqueous sucrose mixtures, measured by various methods at concentrations of 60–80 wt % and temperatures between 0 and 90 °C, were published by Landt in the 1950s,^{34,35} where he observed deviations as large as 6.9% between his data and those reported in Circular 440.³³

During the period of 1947–1952, Swindells *et al.*³⁶ performed a critical study of calibration of viscometers identical to those used previously.³³ The results of this work led to the set of sucrose viscosity data prepared for a NBS publication³⁷ in 1958. These NBS tables are recalculated values of the viscosity of sucrose solutions from NBS Circular 440 after the redetermination of the absolute viscosity of water at 20 °C. The reported values are estimated to be accurate to about $\pm 0.1\%$ in the concentration range of 20–75 wt % between 15 and 25 °C. As mentioned above in

reference to NBS Circular 440,³³ there were no references to the equations used to interpolate and extrapolate the viscosity data over the range of temperatures and concentrations reported. Moreover, according to current NIST staff,³⁸ no records of the original measured data points can be found.

The International Commission for Uniform Methods of Sugar Analysis adopted as standard values of the viscosity of aqueous sucrose solutions those published by Swindells *et al.*,³⁷ along with the data reported by Schneider *et al.*³⁹ up to concentrations of 86 wt %. These data were compiled by Reiser *et al.*⁴⁰ in a review on the properties of sucrose.

The work by Schneider *et al.*³⁹ was the first performed on sucrose solutions by using a rotational viscometer and the reported uncertainty in the viscosity measurements at 20 °C ranges from 0.035% to 0.11% for concentrations between 20 and 70 wt %, respectively.

Very few studies have been performed since the study of Schneider *et al.*³⁹ in order to extend the viscosity measurements of sucrose solutions over a wider range of temperature and concentration. Bellows and King⁴¹ reported viscosity data of sucrose solutions of 70 and 75 wt % at temperatures down to –30 °C using a falling-sphere viscometer. Unfortunately, these data were only reported in graphical form and the uncertainties were not indicated.

James *et al.*⁴² reported high precision viscosity data for 20, 30, and 40 wt % sucrose solutions at 25 °C using a glass viscometer with an extensively flared capillary.

More recently, Kerr and Reid⁴³ measured the viscosity of 20–70 wt % sucrose solutions on the melting curve, that is, at temperatures between –2 and –20 °C (see Table 1) with a rotational viscometer. These authors reported viscosities in the form of Arrhenius, WLF, and power-law plots and also tabulated the coefficients of the WLF and power-law equations for different choices of the glass transition temperature (T_g) and the viscosity of the solution at T_g . The authors claim that the temperature control was ± 0.5 °C and that the concentration of the solutions could have changed between 1% and 2% during the measurements, which in turn produces an uncertainty in the viscosity as large as 100%.

Christoph *et al.*⁴⁴ measured the viscosity of sucrose solutions in the range of 60–75 wt % at temperatures between 5 and 130 °C using a rotational viscometer and performed a detailed analysis of the non-Newtonian behavior of the concentrated solutions. Curiously, no other authors have found this kind of hydrodynamic behavior in concentrated aqueous sucrose solutions.

Hydrolysis and browning reactions seem to not affect the results reported by these authors, who claimed that the sucrose concentration was maintained during the experiments, with a maximum variation of 0.2 wt %. However, the experimental viscosity values obtained were not reported but only an equation which relates $\ln \eta$ to the sucrose concentration and the solution temperature in the range of temperature of 30–130 °C.

Rampp *et al.*⁴⁵ extended the published viscosity measurements into the subzero region at concentrations up to 80.1 wt % (see Table 1) using a rotational viscometer with an

TABLE 1. Sources of viscosity data for sucrose and trehalose aqueous solutions

Reference	Concentration (wt %)	Temperature t (°C)	Range of T_g/T	Number of data (supercooled)
Sucrose				
28	20–60	0 to 95	0.405–0.647	32 (0)
29	65–76	25 to 70	0.617–0.723	48 (29)
30,31	60–80	20 to 90	0.519–0.725	114 (27)
32	20–40	25	0.487–0.536	2 (0)
37	30–75	0 to 35	0.492–0.726	49 (10)
39	40–86	5 to 80	0.494–0.893	152 (120)
41	70–75	–30 to 5.5	0.722–0.876	10 ^a (10)
42	20–40	25	0.487–0.536	3 (0)
43	20–70	–20 to –2	...	8 ^a
45	10.0–80.1	–17.3 to 60	0.461–0.863	70 (33)
46	14.6–60.6	25	0.476–0.618	9 (0)
27	1–60	5 to 60	0.462–0.625	8 (0)
47	70.0–85.2	0 to 90	0.570–0.837	37 (31)
Trehalose				
49	39.2–72.5	–24 to 20	0.558–0.887	21 (20)
50	38.3–74.6	–20 to 85	0.461–0.901	54 (33)
51	6.6–48.7	20 to 85	0.387–0.597	28 ^a
52	3.7–48.7	20 to 85	0.382–0.597	36 (1)
53	6.6–48.7	3 to 85	0.387–0.634	42 ^a
54	6.0–50.0	40 to 70	0.403–0.565	12 ^a
55	5.1–53.7	20 to 80	0.390–0.622	78 ^a (8)
56	20.0–75.0	25	0.493–0.769	15 ^b (12)
57	10.0–50.0	0 to 50	0.463–0.648	14 (3)

^aNumerical data not provided.^bContaining 0.01 M NaCl or LiCl.

average uncertainty of $\pm 0.5\%$. Chenlo *et al.*⁴⁶ reported the kinematic viscosities of aqueous sucrose solutions at concentrations between 14.6 and 60.6 wt % in the temperature range of 20–50 °C using an Ubbelohde viscometer with an uncertainty of $\pm 0.2\%$. As these authors reported the densities of the solutions only at 25 °C, the dynamic viscosity of aqueous sucrose was calculated and analyzed only at this temperature.

The only study on the effect of pressure on the viscosity of aqueous sucrose solutions was performed by Först *et al.*,²⁷ who measured the viscosity of sucrose solutions between 1 and 60 wt % at temperatures between 5 and 60 °C and pressures up to 700 MPa using a rolling-sphere viscometer. The uncertainty in the viscosity data was not reported.

Finally, Quintas *et al.*⁴⁷ measured the viscosity of very concentrated sucrose solutions in the temperature range of 0–90 °C using a stress rheometer. They reported uncertainties in the viscosity measurements ranging from 0.2% to 2.1%.

In order to compare all the sources of viscosity data, we have plotted in Fig. 4 $\log_{10} \eta$ as a function of temperature for several concentrations ranging from 20 to 86 wt % sucrose. The data by Christoph *et al.*⁴⁴ were not taken into account since the experimental viscosity data were not reported and due to doubts about the non-Newtonian behavior claimed by the authors. The data by Chenlo *et al.*⁴⁶ are not plotted in Fig. 4 since they do not correspond to rounded concentrations.

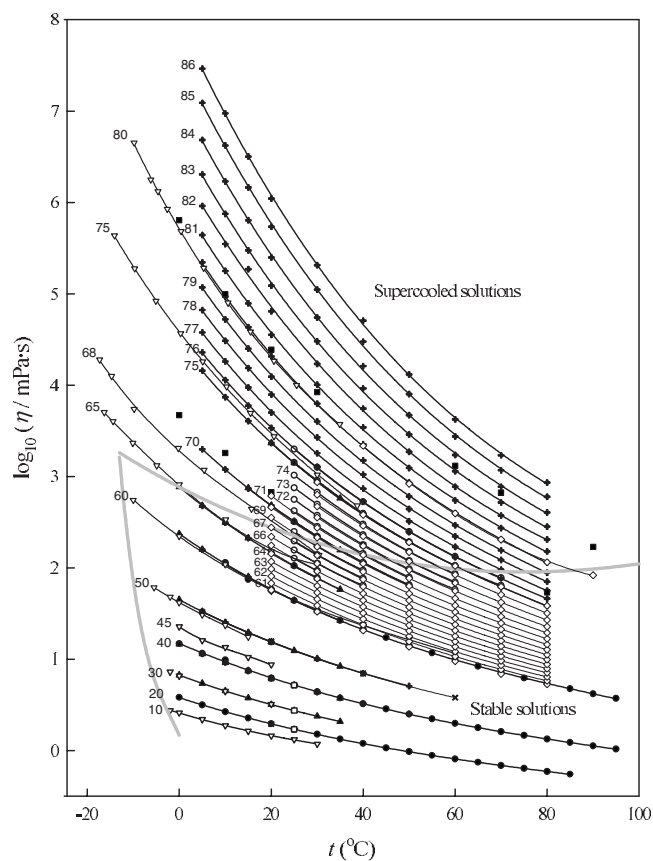


FIG. 4. Viscosity temperature dependence of aqueous sucrose solutions at different sugar concentrations, indicated in wt% on each curve: (x) Först *et al.*,²⁷ (●) Bingham and Jackson,²⁸ (○) Bennett and Nees,²⁹ (◇) Landt,^{30,31} (★) Jones and Stauffer,³² (▲) Swindells *et al.*,³⁷ (+) Schneider *et al.*,³⁹ (□) James *et al.*,⁴² (▽) Ramp *et al.*,⁴⁵ and (■) Quintas *et al.*⁴⁷ The gray lines show the boundary between unsaturated and supercooled solutions.

The viscosity data extend over more than seven orders of magnitude and the agreement among the different sources is, generally speaking, quite reasonable. However, some discrepancies can be observed. For instance, the measurements by Quintas *et al.*⁴⁷ for 69.97 and 79.93 wt % sucrose solutions deviate systematically from those of other authors for the same concentrations and exhibit unusual temperature dependence. For this reason, these data were not considered in our analysis.

Data reported by Bingham and Jackson²⁸ and Bennett and Nees²⁹ were multiplied by 0.996 617 to take into account the difference between the viscosity of water at 20 °C used by the authors ($\eta_w = 1.005$ mPa s) and the reference value recently established ($\eta_w = 1.0016$ mPa s).⁴⁸ A similar correction was performed on the data reported by Swindells *et al.*³⁷ and James *et al.*,⁴² who used a different value for the viscosity of water at 20 °C ($\eta_w = 1.002$ mPa s).

3.2. Aqueous Trehalose

The sources of viscosity data for aqueous solutions of trehalose are fewer than those for sucrose. Only six works have been reported on this system, as summarized in Table 1.

TABLE 2. Coefficients of the Génotelle equation (12) and standard deviation of the fit of sucrose and trehalose aqueous solutions viscosity data with $\eta^* = 1$ mPa s

Coefficient	a_1	a_2	b_1	b_2	n	s
Sucrose (this work)	-0.1245 ± 0.0029	22.452 ± 0.023	1.095 ± 0.026	46.39 ± 0.84	1.303 ± 0.013	0.029
Sucrose ^a (this work)	-0.1253 ± 0.0025	22.467 ± 0.020	1.082 ± 0.022	46.16 ± 0.71	1.296 ± 0.011	0.024
Sucrose (Ref. 12)	-0.114	22.46	1.1	43.1	1.25	0.012
Trehalose (this work)	-0.159 ± 0.019	26.40 ± 0.35	1.31 ± 0.14	30.9 ± 8.1	1.20 ± 0.14	0.099

^aEliminating data which deviate by more than 3σ .

The first study on the viscosity of aqueous solutions of trehalose in the one-phase and the supercooled regions is that by Miller *et al.*,⁴⁹ who used a stress rheometer with parallel plate geometry and reported viscosity data with an uncertainty of approximately $\pm 5\%$ for supercooled solutions. Later, these authors measured the viscosity of trehalose solutions at higher temperatures⁵⁰ by using a stress rheometer with a coaxial cylinder measurement geometry. In this case, the uncertainties were around 0.5% in the supercooled range and about 0.1% in the normal liquid region.

Magazù and co-workers^{51–54} used a capillary viscometer to study moderately concentrated trehalose solutions (below 50 wt %) at temperatures above 20 °C. The accuracy of the measurements was not indicated but it is expected to be better than 0.2%. Tabulated viscosity data were only reported in one of the four works published by the authors.⁵²

Elias and Elias⁵⁵ determined the viscosity of trehalose aqueous solutions over a similar range of concentrations and temperatures with an Ubbelohde capillary viscometer with an uncertainty smaller than 0.1%. However, these authors did not provide numerical viscosity data but reported the parameters of the VTF equation for each of the studied solutions.

Later, Miller *et al.*⁵⁶ measured the viscosity of concentrated trehalose solutions over a wide concentration range (20–75 wt %) at 25 °C with a rotational viscometer. In this case, the studied solutions contained around 0.01 M of NaCl or LiCl but, as the effect of the salt on the viscosity of sugar solutions at this salt concentration can be neglected [at 25 °C, the increment produced in the viscosity by the addition of 0.5 mol kg⁻¹ of NaCl to aqueous solutions with sucrose concentrations between 14.5 and 60.6 wt % is smaller than 6.2% (Ref. 46)], these data were considered in our analysis.

Rampp *et al.*⁵⁷ measured the viscosity of trehalose solutions up to 50 wt % over an intermediate range of temperatures with a rotational viscometer. The uncertainty in these measurements is $\pm 0.5\%$.

Plots similar to that shown for sucrose in Fig. 4 are not possible in this case since the concentrations of the measured viscosity data of trehalose aqueous solutions were often not at rounded values. For the analysis of aqueous trehalose, all viscosity data reported in numerical form were considered.

Tabulations of the data from these sources for sucrose and trehalose aqueous solutions are given in the supplementary material.⁵⁸

4. Data Analysis

In this section, the data for sucrose and trehalose aqueous solutions will be analyzed using some of the equations reviewed in Sec. 2, particularly those which describe the temperature and concentration dependences of the viscosity, and with a new equation that implicitly includes the concentration dependence through a reduced temperature which measures how far the system is from the glass transition point.

4.1. Génotelle Equation

Without a doubt, the sucrose-water system is one of the most studied and it is a reference system for the study of the viscosity of aqueous solutions. As mentioned above, the Génotelle equation (12) was used successfully to describe the viscosity temperature and concentration dependences of concentrated sucrose solutions over a wide range of concentrations and temperatures, including the supercooled region. This region, as shown in Fig. 2, can be reached by increasing the sugar concentration isothermally or by decreasing the temperature at constant concentration.

In Table 2, we summarize the parameters of Eq. (12) obtained by Génotelle¹² using the data available for aqueous sucrose solutions before 1978, that is, those reported in Circular 440 and its supplement^{36,37} and by Schneider *et al.*³⁹ We also report the parameters obtained when the more recent data are included in the analysis. We excluded from this analysis the viscosity data reported by Bellows and King⁴¹ and Kerr and Reid⁴³ due to the fact that these data were reported only in graphical form. Data reported by Christoph *et al.*⁴⁴ were also excluded due to the doubts mentioned in Sec. 3.1. The data included in our analysis correspond only to tabulated viscosity measurements. Only the measured viscosity values reported by Bingham and Jackson²⁸ were included in this fit, while the interpolated or extrapolated ones were excluded.

In Fig. 5, we plot the residuals from a fit of the experimental viscosity data of sucrose solutions with the Génotelle equation as a function of the reduced temperature (T_g/T) in

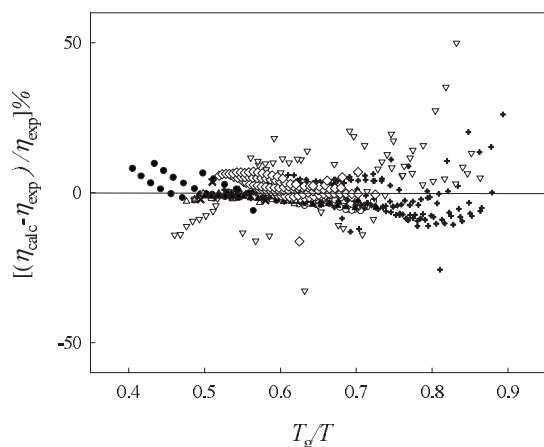


FIG. 5. Deviation plot for the viscosity representation of aqueous sucrose solutions with the Génotelle equation (12). The symbols used are the same as those in Fig. 4 and (Δ) corresponds to data reported by Chenlo *et al.*⁴⁶

order to compare these results to those reported in Sec. 4.2. Some results, such as those from Bingham and Jackson²⁸ and Landt,^{30,31} seem to deviate systematically from the calculated values. However, the absolute value of the maximum deviation in $\log_{10} \eta$ is relatively small, 0.18 units. The fit was improved by eliminating those data that deviated from the calculated values by more than three standard deviations. The resulting fitting parameters are shown in Table 2.

In the case of trehalose, the parameters of Eq. (12), shown in Table 2, indicate that the standard deviation is higher than that obtained for sucrose solutions.

Some residuals of sucrose-water viscosity data exceed three standard deviations, with a maximum deviation of 0.18 units in $\log_{10} \eta$, while for trehalose (Fig. 6), the maximum deviation in $\log_{10} \eta$ is equal to 0.28 units, which is slightly less than three standard deviations.

4.2. Scaled Arrhenius Representation

The scaled Arrhenius representation of the viscosity of aqueous solutions was first introduced by Angell *et al.*,⁵⁹

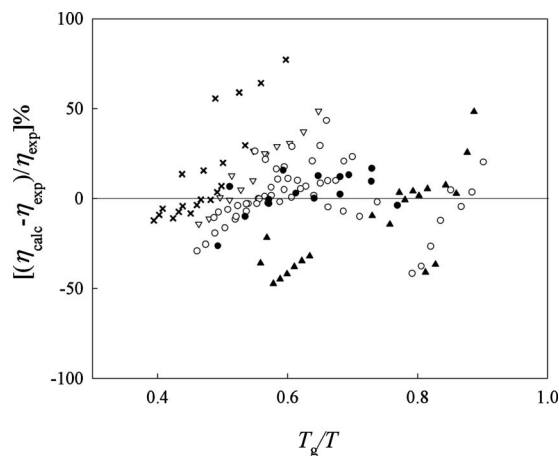


FIG. 6. Deviation plot for the viscosity representation of aqueous trehalose solutions with the Génotelle equation (12). Viscosity data are reported by (\blacktriangle) Miller *et al.*,⁴⁹ (\circ) Miller *et al.*,⁵⁰ (\times) Magazú *et al.*,⁵² (\bullet) Miller *et al.*,⁵⁶ and (∇) Ramp *et al.*⁵⁷

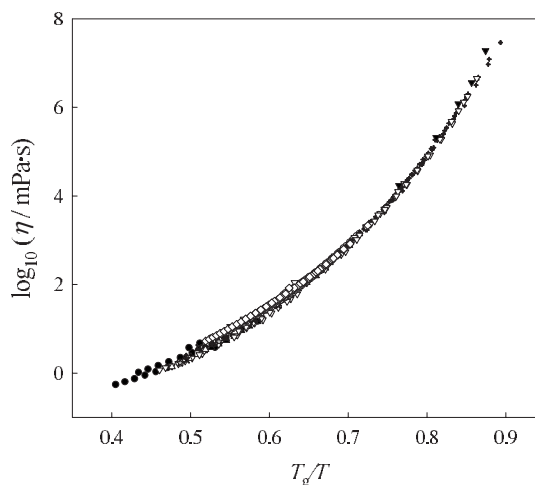


FIG. 7. Scaled Arrhenius representation of the viscosity of aqueous sucrose solutions. The symbols used are the same as those in Fig. 5 and (\blacktriangledown) corresponds to the data reported by Bellows and King⁴¹ in graphical form.

emphasizing that “the glass transition temperature provides an appropriate scaling temperature for corresponding-states comparisons.” They have shown how scaled Arrhenius plots ($\log_{10} \eta$ vs T_g/T) for several polyols, including the saccharides sucrose, glucose, and fructose, seem to merge in a common line in spite of differences in composition and concentration.

We have analyzed in more detail this corresponding-states idea, stressing the dependence of the scaling or reduced temperature, T_g/T , on the composition of a given sugar. In Table 1, we summarize the range of T_g/T analyzed for sucrose and trehalose aqueous solutions to demonstrate that the available experimental viscosity data for the aqueous solutions of these compounds cover a wide range of scaling temperatures, roughly speaking, between 0.4 and 0.9.

The main point of this approach is to assume that for each solute, the effect of its concentration on the viscosity is implicitly taken into account by T_g/T , which determines the distance of the system to the glass transition point. Figures 7 and 8, for sucrose and trehalose, respectively, show that this assumption is reasonable, especially in the supercooled regime or at T_g/T values higher than 0.65.

For both disaccharides, we fitted $\log_{10} \eta$ as a polynomial of T_g/T and found that a cubic equation of the form

$$\log_{10} \frac{\eta}{\eta^*} = a + b \left(\frac{T_g}{T} \right) + c \left(\frac{T_g}{T} \right)^2 + d \left(\frac{T_g}{T} \right)^3 \quad (14)$$

is adequate to represent the viscosity of the solutions with constants a – d as shown in Table 3.

In Fig. 9, we compare the scaled Arrhenius representation of the viscosity data for sucrose and trehalose aqueous solutions to stress the fact that both curves tend to merge in the normal liquid region, but they separate from each other in the supercooled regime ($T_g/T > 0.65$) where the difference in the fragility of the aqueous sugar solutions becomes evident.

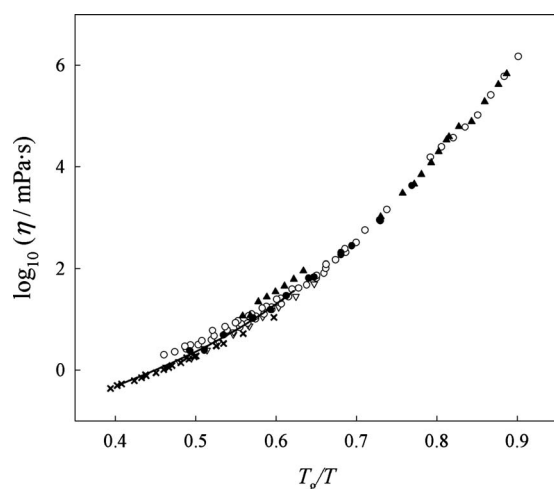


FIG. 8. Scaled Arrhenius representation of the viscosity of aqueous trehalose solutions. The symbols used are the same as in Fig. 6 and the line corresponds to data reported by Elias and Elias,⁵⁵ who gave the parameters of the VTF equation for the viscosity temperature dependence.

Figures 10 and 11 show the deviation plots for the viscosity representation of sucrose and trehalose aqueous solutions with Eq. (14), respectively.

It can be observed in Tables 2 and 3 that the standard deviation corresponding to the viscosity data fitted with Eq. (14) is higher than that corresponding to Eq. (12) for aqueous sucrose solutions, while both equations yield similar standard deviations for trehalose solutions.

Figure 10 also indicates that the residuals from the sucrose-water viscosity data fitted to Eq. (14) exhibit a rather systematic behavior. This can be explained considering that, at low T_g/T values, $\log_{10} \eta$ at constant T_g/T varies slightly with sugar concentration. As this systematic deviation is not observed in the supercooled regime, Eq. (14) can be used to describe, in a better way, the viscosity temperature and concentration dependences in this region.

The resulting parameters of these fits for sucrose and trehalose are summarized in Table 3. Alternatively, the coefficients corresponding to fits of experimental data with a quadratic equation ($d=0$) are also reported. It can be noted that, in the supercooled regime, the quadratic fit yields the same standard deviation as the cubic and should be preferred.

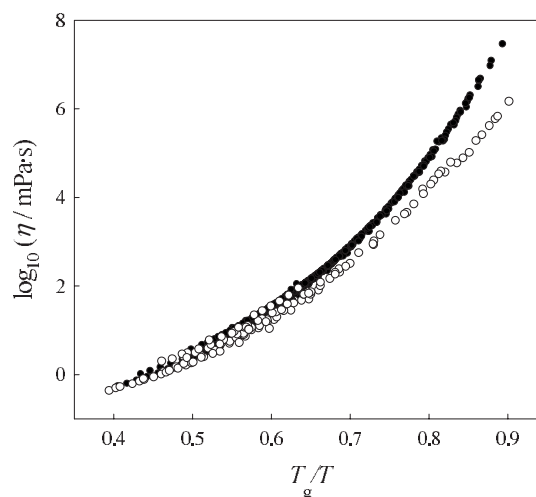


FIG. 9. Comparison of the scaled Arrhenius representations of the viscosity of sucrose and trehalose aqueous solutions.

In Fig. 8, we also include data by Elias and Elias⁵⁵ who gave parameters of the VTF equation for trehalose solutions in the temperature range of 20–80 °C, covering a T_g/T range between 0.39 and 0.62. These authors plotted the viscosity data in the T_g -scaled Arrhenius form, covering a reduced T_g/T interval, and concluded that all the solutions in the interval between 5 and 54 wt % fall on the same curve. The results in Fig. 8 show that this is valid for the entire range of reduced temperature of $0.4 < T_g/T < 0.9$.

An important point in this corresponding-states description of the viscosity is the way we assign the glass transition temperature of the sugar solutions as a function of sugar concentration. For this assignment, we used the Gordon–Taylor equation⁶⁰

$$T_g = \frac{w_1 T_{g1} + w_2 k_{GT} T_{g2}}{w_1 + w_2 k_{GT}}, \quad (15)$$

where w_1 and w_2 are the weight fractions of solute and water, respectively, and T_{g1} and T_{g2} are the glass transition temperatures of pure saccharide and pure water, respectively. The coefficient k_{GT} can be calculated from the densities of the components and the change in the thermal expansibility at T_g but, in practice, it is an adjustable parameter. In Table 4, we

TABLE 3. Coefficients of the scaled Arrhenius equation (14) and standard deviation of the fit of sucrose and trehalose aqueous solutions viscosity data with $\eta^* = 1$ mPa·s (the number of significant digits reported for fitted parameters exceeds the standard error to insure that fitted equations can be reproduced)

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>s</i>
Sucrose	-5.7560 ± 0.5162	23.7453 ± 2.4309	-38.9457 ± 3.7622	32.4121 ± 1.9129	0.059
	2.8227 ± 0.1268	-17.1104 ± 0.3892	24.6772 ± 0.2949	...	0.075
Sucrose ^a	-0.6879 ± 3.3189	5.8606 ± 13.3484	-18.3834 ± 17.8218	24.7438 ± 7.8987	0.032
	9.6680 ± 0.3009	-35.8810 ± 0.8107	37.4210 ± 0.5426	...	0.032
Trehalose	-1.5893 ± 1.0846	1.7811 ± 5.2906	0.2401 ± 8.4159	8.1614 ± 4.3584	0.103
	0.3956 ± 0.2322	-8.0321 ± 0.7337	15.9649 ± 0.5626	...	0.104
Trehalose ^a	12.6256 ± 6.1677	-58.1044 ± 25.9777	83.3907 ± 36.1309	-29.8973 ± 16.5960	0.100
	1.6002 ± 0.7772	-11.4675 ± 2.1912	18.3572 ± 1.5172	...	0.102

^aFit corresponding to the supercooled regime.

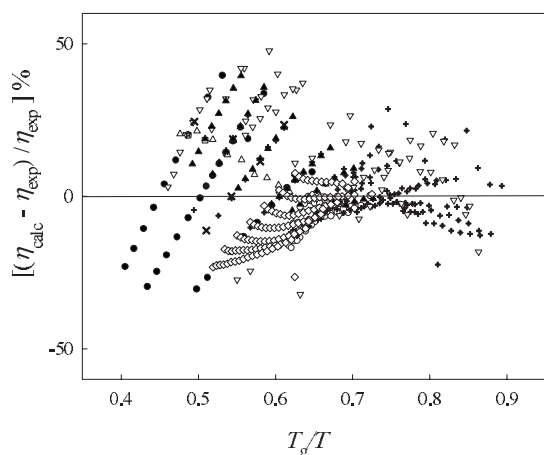


FIG. 10. Deviation plot for the viscosity representation of aqueous sucrose solutions with Eq. (14). Viscosity data in this figure have the same symbols as those in Fig. 5.

summarize the values of the parameters used in this work to calculate T_g of the disaccharide solutions, which are close to those reported in the literature.^{61–63}

For this calculation, we used onset T_g values of aqueous sucrose mixtures reported by Luyet and Rasmussen,⁶⁴ Shalaev,⁶⁵ Green and Angell,⁶⁶ Roos,⁶⁷ Roos and Karel,⁶⁸ Izzard *et al.*,⁶⁹ Mackenzie,⁷⁰ Ottenhof *et al.*,⁷¹ and Goff.⁷² For aqueous trehalose solutions, midpoint T_g values reported by Miller *et al.*^{49,50} and Saleki-Gerhardt⁷³ were the only data included in the fit.

For the analysis performed in this work, the T_g data reported in the literature were carefully selected considering the uncertainties in the values reported by the different authors. The parameters of the Gordon and Taylor equation that we have obtained have smaller uncertainties than those calculated by other authors.^{62,63,74}

It should be emphasized that the choice of the equation to calculate T_g of the aqueous solutions is not critical for the scaled Arrhenius representation of the solution viscosity. Any other reasonable choice for estimating T_g of these solutions,

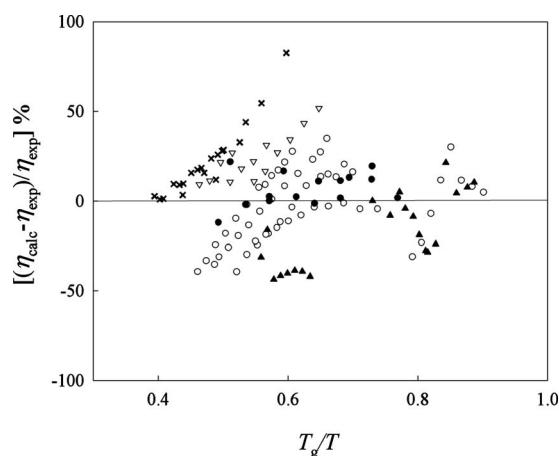


FIG. 11. Deviation plot for the viscosity representation of aqueous trehalose solutions with Eq. (14). Viscosity data in this figure have the same symbols as those in Fig. 6.

TABLE 4. Parameters of the Gordon–Taylor equation for T_g values of sucrose and trehalose aqueous solutions

	T_{g1} (K)	T_{g2} (K)	k_{GT}
Sucrose	336	135	4.74 ± 0.07
Trehalose	388	135	5.04 ± 0.04

which leads to uncertainties on the order of the experimental errors (2–3 K), does not alter the validity of Eq. (14) but only results in different values of the fitting coefficients.

4.3. Comparison with Other Equations

Finally, we compare our descriptions of the viscosity of sucrose and trehalose aqueous solutions to others already reported in the literature for sucrose and trehalose based on a more restricted set of experimental data than that considered in this work or for solutions containing additional solutes.

The linearized form of the WLF equation (6) was introduced by Kerr and Reid:⁴³

$$\frac{(T - T_g)}{\log_{10}(\eta/\eta_g)} = -\frac{C_2}{C_1} - \frac{1}{C_1}(T - T_g), \quad (16)$$

and they found that for sucrose, glucose, and maltodextrin solutions, at temperatures up to 50 K above T_g , all the viscosity data could be represented with Eq. (16) with $C_1 = 16.5$, $C_2 = 37.5$, and $\eta_g = 10^{12}$ Pa s.

Soesanto and Williams¹⁷ employed the WLF equation (6) for the description of concentrated solutions of sucrose and fructose blends. They recognized that the viscosity at the glass transition temperature should be a function of the composition of the mixture.

Miller *et al.*⁵⁰ used the same approach to describe aqueous trehalose solutions with the linearized WLF equation (16). They analyzed all their viscosity values for aqueous trehalose and trehalose/borate mixtures and found that all viscosity data could be well represented with the WLF equation in two temperature regions: $T < T_g + 45$ K and $T > T_g + 45$ K, with $C_1 = 12.5$ and $C_2 = 15.8$ for $T < T_g + 45$ K and $C_1 = 14.9$ and $C_2 = 27.3$ for $T > T_g + 45$ K. However, deviations as large as 0.9 units in $\log_{10} \eta$ could be obtained when viscosity is calculated with these C_1 and C_2 values. They also analyzed viscosity data with the WLF equation as a function of temperature at fixed trehalose concentrations and observed that C_1 varies between 15.5 and 12.1 and C_2 varies between 11.9 and 26.3 for trehalose concentrations between 38.3 and 74.6 wt %, with a dramatic improvement in the fitting.

Following the same procedure for aqueous sucrose mixtures at concentrations between 10 and 86 wt % sucrose, it was observed that, fitting all viscosity data for $T < T_g + 45$ K and $T > T_g + 45$ K, values of $C_1 = 15.3$ and 17.9 and $C_2 = 37.5$ and 51.9 are obtained for each temperature range. This procedure gives differences between experimental and calculated viscosity data as large as 0.8 units in $\log_{10} \eta$. When viscosity data are analyzed with the WLF equation as a function of temperature at fixed sugar concentrations, it can

be observed that C_1 varies between 15.7 and 16.3 and C_2 varies between 20.5 and 43.7 for sucrose concentrations between 10 and 86 wt % and the fit improves considerably, as noted for trehalose solutions. Therefore, it can be concluded that the WLF equation gives an accurate description of the temperature dependence of the viscosity data, but it fails to describe both the temperature and concentration dependences.

The power-law equation (7) was also tested for aqueous trehalose solutions⁵⁰ and it was concluded that, at temperatures more than 20 K above T_c , it describes quite well the viscosities of the trehalose solutions at concentrations between 38.3 and 74.6 wt %. If T_c is fixed at $1.18T_g$, the parameter η_0 in Eq. (7) varies from 1×10^5 to 3×10^5 Pa s in this range of concentration, while the power exponent γ decreases slightly from -3.55 to -3.65 when the concentration increases.

Following the same procedure for aqueous sucrose solutions, it was observed that η_0 varies between 7×10^3 and 8×10^7 Pa s and γ varies between -3.14 and -4.66 for sucrose concentrations between 10 and 75 wt %. Therefore, it can be concluded that a general description of the viscosity temperature and concentration dependence for $T > T_c$ cannot be given with the power-law equation.

Quintas *et al.*⁴⁷ analyzed the effect of sucrose concentration on the WLF equation in the supercooled regime (concentrations in the range of 70–85 wt %). They found that C_1 is dependent on the concentration, whereas C_2 does not show statistically significant concentration dependence. However, this conclusion is doubtful in view of the systematic deviations observed in the viscosity data reported by these authors in concentrated aqueous solutions. In the fit performed with the WLF equation in this work, for sucrose-water mixtures at different concentrations, it was observed that C_2 varies more than C_1 for sucrose concentrations between 10 and 86 wt %, in disagreement with the observations of Quintas *et al.*⁴⁷ It should be mentioned that in this work, η_g concentration dependence was taken into account, as suggested by Soesanto and Williams.¹⁷

The random-walk model proposed by Arkhipov and Bässler^{22,23} was tested by Quintas *et al.*⁷⁵ using their data for very concentrated (80–85 wt %) aqueous sucrose solutions.⁴⁷ These data covered the supercooled region in the high-temperature ($T > T_c$) range, so they used Eq. (10) and found that it is possible to give the viscosity temperature dependence in this region, when the three fitting parameters (η_0 , T_0 , and α) depend on concentration. The comparison of the fit with Eq. (10) and the experimental data clearly shows that the random-walk model with three concentration-dependent parameters would overestimate the viscosity of the supercooled sucrose solutions at temperatures higher than those used in the fitting. The general picture that emerges from Fig. 12, taken from the data reported by the authors,⁷⁵ is that the viscosity of the aqueous sucrose solutions predicted by Eq. (10) is almost independent of concentration in the interval $T_g/T > 0.75$, but there is very pronounced concentration dependence below that limit. For instance, at

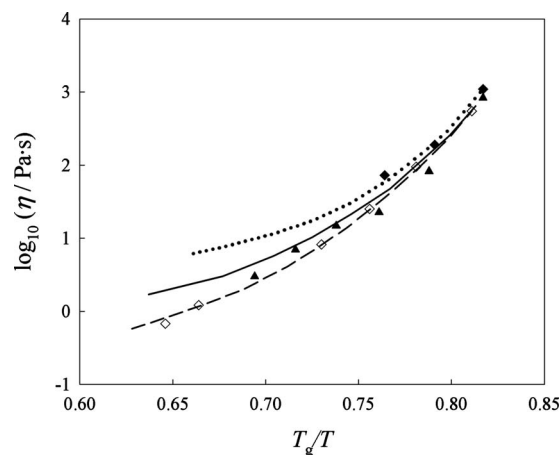


FIG. 12. Scaled Arrhenius representation of the viscosity of aqueous sucrose solutions compared to the results of the random-walk model⁷⁵ at three concentrations. Experimental viscosity values for sucrose at (\diamond) 79.9 wt %, (\blacktriangle) 82.9 wt %, and (\blacklozenge) 85.2 wt % and viscosity reduced temperature dependence obtained with the random-walk model for sucrose at (-----) 79.9 wt %, (—) 82.9 wt %, and (·····) 85.2 wt %.

$T_g/T=0.65$, the viscosity of 80 and 85 wt % sucrose solutions would differ by more than an order of magnitude, which was not observed for the experimental data reported in Fig. 7.

The plots of $\log_{10} \eta$ vs T_g/T (Fig. 12) reported by Quintas *et al.*⁷⁵ confirm that the T_g -scaled Arrhenius representation provides a much simpler description of both the temperature and concentration dependences of the solution viscosity in the supercooled regime, even when the quality of the experimental data reported by these authors is questionable.

Finally, it is worthwhile to analyze the extended Vand equation (13) proposed by Först *et al.*²⁷ to describe the concentration and temperature dependences of sucrose solutions. As mentioned in Sec. 2.3, the viscosity data for aqueous sucrose solutions in the temperature range of 20–80 °C, taken from the compilation by Mageean *et al.*,⁷⁶ can be described very well with Eq. (13) at ambient pressure.

These authors also concluded that Eq. (13) can be extended to predict the viscosity of sucrose solutions at high pressures. For this purpose, they used the relative viscosity in Eq. (13) with the form $\eta_r(T,p) = \eta(T,p)/\eta_w(T,p)$, that is, referred to the viscosity of water at the same pressure as the solution. Furthermore, they calculated the pressure-dependent volume concentration $v(T,p)$ by using the mass fraction, w , and the density, $\rho(T,p)$, of the solution [$v(T,p) = w\rho(T,p)$]. A change in $\eta_r(T,p)$ can be achieved by changing the solute concentration or pressure.

The results, shown in Fig. 13, indicate that the extended Vand equation (13) provides an excellent viscosity description not only of the temperature and concentration dependences but also of the pressure dependence. The relative viscosity change with sucrose concentration at constant pressure coincides with the pressure dependence at fixed sucrose concentration. Thus, at 20 °C and 50 wt % sucrose, a pressure increase from 0.1 to 700 MPa is equivalent to an increase in sucrose concentration to 56 wt % at ambient pressure. In

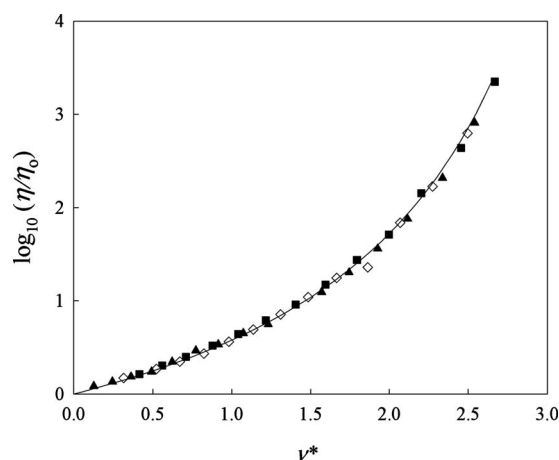


FIG. 13. Viscosity of aqueous sucrose solutions at high pressures fitted with the extended Vand equation (13). Viscosity values at (■) 20 °C, (◇) 40 °C, and (▲) 60 °C. The line corresponds to the viscosity calculation performed with Eq. (13) with $q_1 = -0.248$.

other words, the coefficients q_0^* and q_1 , which can be easily determined from ambient pressure viscosity and density data, are independent of pressure.

One is tempted to compare this pressure behavior to the scaled temperature representation by trying to determine if the viscosity of the sucrose solutions at high pressures could merge on the same curve at the scaled Arrhenius plot with data determined at 0.1 MPa. Unfortunately, lack of information on the pressure dependence of the glass transition temperature of sucrose and trehalose aqueous solutions precludes us from performing such extension of Eq. (14) for high pressures.

5. Conclusions

All the available experimental data on the viscosity of concentrated (>10 wt %) aqueous solutions of trehalose and sucrose were analyzed over a wide range of concentrations and temperatures covering the normal liquid and the supercooled liquid regions, close to the glass transition temperature.

A detailed discussion of the data sources was presented, including the experimental methods employed for viscosity determination and the accuracy of each data set, when reported. These sugar solutions are fragile systems, that is, their viscosity temperature dependence exhibits a large departure from Arrhenius behavior. Several empirical equations describing the temperature and concentration dependences of the solution viscosity were analyzed, including those which account for both effects simultaneously, such as the Génotelle equation, which provides a quite reasonable fit of the experimental data over a wide range of concentrations and temperatures (more than seven orders of magnitude in viscosity). It was found that a simple form representing the viscosity of the aqueous solutions of these disaccharides could be given in terms of a scaled Arrhenius equation, which adopts the reduced temperature T_g/T as the state variable. This equation seems to describe the viscosity of aque-

ous sucrose and trehalose quite well, particularly in the supercooled region. In the supercooled regime ($T_g/T > 0.65$), the fragility of the aqueous sugar solutions determines the slope of the scaled Arrhenius plots, but the curves merge in the normal liquid region.

A comparison with results obtained using other theoretical or semiempirical equations was also presented. An extension of the Vand equation seems to describe well the effect of pressure on the viscosity of sucrose solutions.

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