Translational Diffusion in Sucrose Solutions in the Vicinity of Their Glass Transition Temperature

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The prediction of the stability of low-moisture products is complex, particularly close to the glass transition temperature. This study demonstrates that the relations used to evaluate the influence of temperature on the viscosity of carbohydrate media cannot be applied to the diffusivity. The translational diffusion coefficient of a fluorescent molecule (fluorescein) is measured in sucrose−water mixtures as a function of temperature. The main result is that the mobility of the fluorescein is not simply coupled to the viscosity of the diffusion medium at temperatures close to the glass transition temperature. Indeed the WLF equation, which gives a good prediction of the viscosity, does not allow the determination of the diffusivity in a temperature range close to T_g because the translational diffusion follows a weaker temperature dependence. Different possible explanations for this apparent decoupling between translational diffusion and viscosity are suggested: a small change in the hydrodynamic radius of the diffusing molecule due to low water content and/or a connection with the β relaxation process.

Introduction

The physical state of the amorphous matrix existing in frozen or dehydrated foods greatly influences their stability, i.e., affects both physical and chemical changes during processing and storage. Deteriorative changes observed in these products, such as stickiness,[1] collapse,[2] crystallization,[3] and chemical and biochemical reactions[4] are mostly controlled by molecular mobility. The importance of the glass transition temperature for the storage stability has been claimed and emphasized by Levine and Slade.[5] The molecular mobility is expected to be strongly dependent on the distance $(T−T_g)$ of the experimental temperature (T) to the glass transition temperature (T_g) of the investigated material. Most amorphous food components are miscible with water, which acts as a plasticizer, causing a decrease in the glass transition temperature with increasing water content. Therefore, the promoting action of an increase in temperature or water content on the kinetics of changes observed in food products during processing and storage may be related to the change in molecular mobility associated with the glass transition. In fact, water has a strong effect on T_g, but its influence on the mobility pattern of solutes may be quite independent of T_g.[6]

Understanding the influence of temperature and water content on molecular mobility is critical for modeling many operations in food engineering. Knowing translational diffusion coefficients (D_{trans}) is particularly necessary. The data, however, are scarce, especially for the temperature domain around T_g, where the determination of D_{trans} in real food is usually intricate and inaccurate.

Our first objective was therefore to develop a method to measure translational diffusion coefficients, applicable also for very low values of these parameters.[7] Given the paucity of diffusion data, it has often been proposed to use the Stokes−Einstein relation (SE) to estimate the variation of D_{trans} as a

function of temperature (T) from the variation of viscosity (η):

$$D_{trans} = \frac{k_B T}{6\pi r \eta} \tag{1}$$

k_B is the Boltzmann constant, T the temperature in Kelvin, r the hydrodynamic radius of the diffusing molecule, and η the viscosity. However, from some recent studies[8−10] with organic glass-forming liquids, it seems that the SE relation may not strictly apply in the vicinity of the glass transition. The purpose of this study was then to compare translational diffusion data with viscosity values in the temperature domain close to T_g for a material of interest in food engineering, i.e., sucrose−water solutions.

Background

The glass transition temperature (T_g) is conventionally the temperature where a change in heat capacity can be detected by differential scanning calorimetry (DSC). The glassy state is characterized by a high viscosity (approximately 10^{12} Pa s at T_g). Above T_g, Arrhenius plots of viscosity data show nonlinearity, which suggests that the temperature dependence of viscosity of supercooled liquids cannot be described by an Arrhenius-like relationship, as is the case above the melting point. The temperature dependence of dynamic properties in the temperature range above the glass transition can be described by several expressions, the most popular being the Vogel−Tammann−Fulcher (VTF)[11−13] and the Williams−Landel−Ferry (WLF)[14] expressions:

$$\eta_T = \eta_0 \exp\frac{BT_0}{(T - T_0)} \tag{2}$$

$$\log\frac{\eta_T}{\eta_{T_g}} = \frac{C_{1g}(T - T_g)}{C_{2g} + (T - T_g)} \tag{3}$$

where η_T and η_{T_g} are viscosities at T and T_g respectively; η_0, B, T_0, C_{1g}, and C_{2g} are phenomenological coefficients. Both

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expressions can be interconverted. They have been shown to satisfactorily describe the viscosity of supercooled liquids of various types,[15,16] as long as T is not too far above T_g.[17]

C_{1g} and C_{2g} are the WLF constants when the reference temperature used in the WLF equation is T_g. Equation 3 is often used with the so-called universal constants: $C_{1g} = -17.4$ and $C_{2g} = 51.6$ K, which have been extracted in early experiments from data on numerous polymers.[14] These universal values allow a first approximation of the viscosity when data on the studied system do not exist in the literature. However, several experiments indicated that these constants could deviate from the universal values depending on the investigated material[17,18] or on the observed phenomena, i.e., viscosity or relaxation time.[18]

The third equation which is also used to predict the viscosity is the power-law equation, resulting from the development of the mode-coupling theory:[19,20]

$$\eta = A(T - T_c)^\gamma \tag{4}$$

with A and γ constants and T_c the so-called critical temperature used as reference. The applicability of this equation is restricted to rather high temperatures, above the temperature T_c, which has been found to be $\approx 1.2 T_g$ for various materials.

The mobility in some organic glass-forming liquids such as *o*-terphenyl (OTP) is well documented in the literature.[10,21] From the experimental determinations of the translational diffusion coefficient, it was shown that the usual Stokes–Einstein equation may not strictly apply in the vicinity of the glass transition.[8-10] A consistent decoupling effect between the viscosity and the translational diffusion was noticed:[22] the translational motions of molecules seemed not to be controlled only by the shear viscosity of the media, but were faster than predicted from this parameter. Parker and Ring[23] reported some experimental translational diffusion coefficient values of water in a carbohydrate matrix as a function of temperature. The results obtained at temperatures around the glass transition of the system could not be predicted from the viscosity of the diffusion medium, derived from the WLF equation. However, the size of the diffusing molecule compared to the size of molecules that compose the matrix of diffusion should be taken into account to predict the rotational or translational diffusivity.[9,10,24] The size effect was also noticed for synthetic polymeric systems such as polystyrene and poly(methyl methacrylate)[25] or bio-macromolecule media like casein.[26] The mechanism controlling the mobility of small molecules may also be a function of the microporosity of the macromolecule (free volume above T_g, size of the defects below the glass transition temperature) and of the characteristics of the polymer structure such as flexibility of the chain.[27] The molecular interactions may also be a consistent parameter affecting mobility; a shift from stick to slip boundary conditions of a molecule in a polar medium should be taken into account for the interpretation of the diffusivity changes.[6] Indeed, most of the reported results were obtained with apolar systems, where van der Waals intermolecular interactions were predominating. The present study was devoted to a system where the diffusing molecule and the matrix have similar molecular weight, but with a predominant H bond network.

Generally, measurements of rotational diffusion are easier to perform than that of translational motion in viscous media. Using electron spin resonance[6] (ESR) or fluorescence anisotropy techniques,[21] the rotational mobility was determined in low water systems or nonpolar media. NMR techniques are more and more often used to study the rotational diffusion coefficients.[9,28] The measurement of the relaxation times T_1 and T_2 by pulsed

NMR allows the determination of the rotational mobility, although the results may be dependent on the model used to fit the experimental data. For translational diffusion, only few techniques allow the measurement of such low mobilities as observed in systems approaching their T_g. Le Meste[24] reviewed them in a recent paper with the mobility range available for each technique. Forced Rayleigh scattering (FRS)[9,25,27,29,30] and fluorescence recovery after photobleaching (FRAP)[31] allow the determination of translational diffusion coefficients of tracers down to 10^{-20} m^2 s^{-1}. NMR techniques are also used, particularly the pulsed gradient spin–echo (PGSE) NMR[29] for measuring self-diffusion coefficients, but they appear to be still restricted to a temperature domain remote from the glass transition.

In this study, the viscosities of sucrose solutions at concentrations from 30% to 65.3% (w/w) were measured from −15 to 20 °C. Translational diffusion coefficients of a small water-soluble dye, fluorescein, were measured in sucrose–water solutions at concentrations from 30% to 90% (w/w) in a range of temperatures from −15 to 30 °C, i.e., in the vicinity of the glass transition temperature for the more concentrated solutions. The translational diffusion coefficient of fluorescein was measured with the fluorescence recovery after photobleaching (FRAP) method, using an interference fringe pattern.[7]

Materials and Methods

Sample Preparation. Coarse-grained sucrose was used as a diffusion medium for a small tracer. The purity of sucrose solutions was checked by liquid-phase chromatography. As no impurity was detected by this method, the coarse-grained sucrose was used without further purification. For dilute solutions, the sucrose was just dissolved under agitation at different concentrations from 30% to 65.3% (w/w) in distilled water. For concentrated solutions from 84% to 90%, a 50% sucrose solution was first prepared and then dehydrated at a temperature lower than 140 °C. Dehydration was performed under heavy agitation in a tube plunging into a temperature-controlled oil bath. The water content of the sample was determined from the loss of mass during the heating process. The viscous sucrose water mixtures were introduced into a spectrometric standard cuvette and put into a cold alcohol bath at a temperature around −10 °C. The rapid decrease in temperature allowed the glass formation from the viscous liquid without any sucrose crystallization.

The diffusing molecule, fluorescein (disodium salt, Kuhlmann) was used in solution in distilled water at final concentrations of 3 μM for dilute sucrose solutions and at 9 μM for dehydrated mixtures. The pH of the solutions was around 7.0.

The Fluorescence Recovery after Photobleaching. The fluorescence recovery after photobleaching method (FRAP) was used to measure translational diffusion coefficients as described in a previous paper[7] and summarized here. The mobile fluorescent molecules were dispersed uniformly in the sample. Using an interference fringe pattern, the FRAP technique allowed the measurements of diffusion over distances smaller than 5 μm. An irreversible photochemical bleach was created with this periodic fringe pattern with a brief intense light pulse. The diffusion coefficients were determined from the rate of fluorescence recovery which results from the transport of the fluorophore from the unbleached to the bleached fringes of the sample. The diffusion coefficient calculation was deduced from Fick's second law and the shape of the exponential fluorescence recovery curve. The detailed explanation of calculations was presented in the previous study.

Viscosity Measurements. The viscosity of sucrose solutions was measured with a rheometer (Rheometer 30, Contraves). The
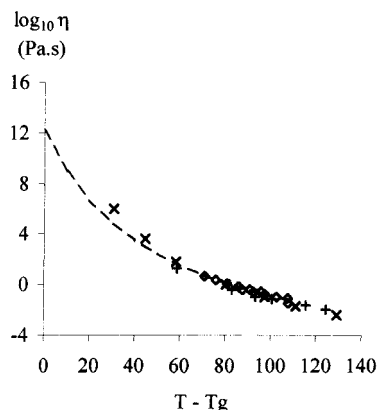
Figure 1. Viscosity of sucrose solutions as a function of the temperature difference $(T-T_g)$. T_g determined with the Gordon–Taylor equation (eq 5). Our viscosity measurements ($\diamond$) are compared with viscosity determinations of Bellows and King[32] (1973) ($\times$) and Kerr and Reid[16] (1994) ($+$). The line represents the WLF equation fitted to our experimental values ($C_{1g} = -19.8$, $C_{2g} = 51.6$ K, and $\eta_{T_g} = 1.6 \; 10^{12}$ Pa s).

Figure 2. Translational diffusion coefficients of fluorescein in sucrose–water mixtures as function of $(T-T_g)$, T_g being calculated from eq 5 for different concentrations: $\diamond$ for 30% sucrose, $\triangle$ 43.5%, $\times$ 57.5%, $\circ$ 65.3%, $\square$ 84%, $*$ 87%, $-$90%. The line represents the WLF equation fitted to the experimental data for the concentration below 85% ($C_{1g} = -17.4$, $C_{2g} = 51.6$, and $D_{T_g} = 8 \times 10^{-24}$ m^2 s^{-1}).

viscosity was monitored as a function of temperature in solutions 45.3%–65.3% (w/w) sucrose, with temperature conditions avoiding the formation of ice, i.e., from −15 to 20 °C. A temperature-controlled alcohol bath maintained a constant temperature during the experiments.

Results

The viscosity and the translational diffusion coefficient were measured for different sucrose solutions as a function of temperature. Every result was plotted using as a reference the glass transition temperature of the corresponding solution. The T_g values were the T_g onset calculated from the Gordon–Taylor equation:

$$T_g = \frac{w_s T_{g_s} + k w_w T_{g_w}}{w_s + k w_w} \qquad (5)$$

where w_s, w_w, T_{g_s} and T_{g_w} are respectively the mass fraction and the onset glass transition temperatures of pure sucrose and water. The values of T_{g_s} and T_{g_w} used are 338 and 135 K, respectively. The k value (5.46) was obtained by the fit of eq 5 to experimental T_g values for different sucrose concentrations, which were determined from differential scanning calorimetry curves (heating/cooling rate: 10 K min^{-1}).[32]

Experimental Results. Figure 1 shows the viscosity values for different sucrose solutions as a function of the difference between the measurement temperature (T) and the glass transition temperature (T_g). Some experimental data found in the literature were also plotted on the same graph.[16,33]

Figure 2 shows a plot of the measured translational diffusion coefficients of fluorescein in sucrose–water mixtures at different concentrations, as a function of the temperature difference $T-T_g$. The translational diffusion values cover a wide range of mobility: over six decades from 10^{-12} m^2 s^{-1} for a 30% sucrose solution at 20 °C to 10^{-18} m^2 s^{-1} for a 90% sucrose at −10 °C. The diffusivity of fluorescein in sucrose solutions decreased as the temperature decreased and as the concentration of the matrix increased.

For highly concentrated sucrose media, the fluorescein diffusion was very low; a complete recovery curve of FRAP required a longer experimental time of 1 or 2 days, which was not achievable with our experimental setup. Only 10% of the whole exponential recovery curve was fitted for the lowest
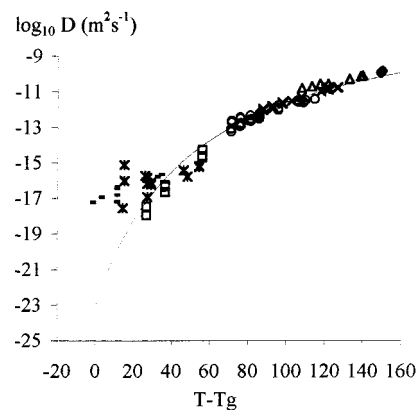
diffusion values, leading to a standard deviation of about 100% on the estimated values of the diffusion coefficients instead of 10% for dilute systems.

For sucrose concentrations higher than 85%, the recovery data could not be fitted with only one exponential curve, so two relaxation times were calculated from two distinct exponential curves. The difference between the two relaxation times never exceeded a factor of 10. The same result was also found with a FRAP technique used to measure the diffusion of a dye tracer in different systems[31,34] and was explained by the degradation of the sample. The need for two exponential recovery curves to fit some FRAP data could be explained by the presence in the system of two populations of fluorescent molecules with different diffusion coefficients. The reversibility of the probe bleaching could also be the reason for having two populations in the samples. The reversibility phenomenon of the fluorescein molecule after bleaching was observed in viscous sucrose solutions by Periasamy et al.[35] If the fluorescent molecule and its photoproduct, the molecule after photobleaching, did not have the same properties, their diffusion coefficients could be different. One could envisage that some spatial heterogeneity could be the reason for having two translational diffusion coefficients. This heterogeneity could be due to a possible water eviction from the matrix before crystallization of the sucrose as described by Mathlouthi.[36] This author explained that at high temperatures in highly concentrated sucrose solutions, the dehydration of the matrix occurs before the sucrose crystallization. Because crystal growth is particularly slow due to the high viscosity of the media, no disturbance by sucrose crystals was observed in the samples, but the possible formation of water-rich regions could explain the higher diffusion coefficient. However, this possible heterogeneity should not allow the measurement of two diffusion values but the observation of only one corresponding to the average translational mobility: the determination of two coefficients would imply that the spatial heterogeneity was very large (at least a few micrometers, the length of the interference fringe pattern) and allowed a fast mobility compared to the concentrated supercooled liquids.

Whatever the reason for having two translational diffusion coefficients, only the lowest diffusion coefficient was taken into account for the discussion of the results, considering the values which were the most likely with regard to the viscosity.

WLF Prediction. The WLF relation was found to characterize well the viscosity at a given temperature in carbohydrate

TABLE 1: Parameters Characterizing the Temperature Dependence Obtained by Fitting the WLF Equation to Our Experimental Data for Diffusion and Viscosity in Sucrose Solutions

	predicted values				
	for viscosity of the matrix			for diffusion of fluorescein	
	WLF prediction $r^2 = 0.98$		SE with η_{WLF}[a]	WLF prediction $r^2 = 0.85$	
fixed values for fitting	WLF coefficients	η_{T_g} Pa s	D_{T_g} m² s⁻¹	WLF coefficients	D_{T_g} m² s⁻¹
$C_{1g} = -17.4$	$C_{2g} = 90.0$	1.9×10^8	$\approx 2 \times 10^{-21}$	$C'_{2g} = 92.0$	2×10^{-21}
$C_{2g} = 51.6$[b]	$C_{1g} = -19.8$	1.6×10^{12}	$\approx 2 \times 10^{-25}$	$C'_{1g} = -17.4$	8×10^{-24}
$\left\{\begin{array}{l}C_{1g} = -17.4\\ C_{2g} = 51.6\end{array}\right.$		4.3×10^{10}	$\approx 8 \times 10^{-24}$		8×10^{-24}
$\eta_{T_g} = 10^{12}$ Pa s	$\left\{\begin{array}{l}C_{1g} = -19.2\\ C_{2g} = 49.6\end{array}\right.$		$\approx 3 \times 10^{-25}$		

[a] From the predicted viscosity values, a mean value of the translational diffusion coefficient at T_g was calculated from the Stokes−Einstein relation (SE) with a fluorescein radius of 5.02 Å (Champion et al., 1995).[7] [b] Fit chosen for the prediction of viscosity.

systems.[15,16,37] Table 1 shows the C_{1g}, C_{2g} values determined from the fit of our viscosity data with eq 3 (Figure 1) for sucrose mixtures in the observed temperature range, from −15 to 20 °C.

The use of eq 3 was extended for synthetic polymers[34,37] or supercooled liquids[25] to the diffusion coefficients in accordance with the Stokes−Einstein relation (SE) between viscosity (η) and diffusion (D_{trans}), resulting in the WLF relation for diffusion:

$$\log\frac{D_{T_g}}{D_T} \approx \frac{C'_{1g}(T - T_g)}{C'_{2g} + (T - T_g)} \tag{6}$$

The fit of our experimental diffusion coefficient values with eq 6 was done for $T_g/T < 0.86$. The values obtained at temperatures between T_g and $1.2T_g$ were left for the prediction with eq 6 and are discussed later in the text. The results of the WLF fits are shown in Table 1. In the temperature domain well above the glass transition, (i.e. $T > T_g + 40$ °C), the WLF relation could also be used to describe the evolution of the translational mobility of a small molecule with temperature. The D_{T_g} obtained by fitting eq 6 to our experimental data agreed well with the values that were calculated using the WLF predicted viscosities and the SE relation (Table 1). This good agreement between diffusivity and viscosity allowed us to conclude that, for $T \geq 1.2T_g$, the combination of SE and WLF equations gave a good prediction for the translational motions of small molecules in a medium composed also of small molecules.

The WLF coefficients obtained from these fits of viscosity and diffusion (Table 1) are not very different from the values of the "universal constants" ($C_{1g} = -17.4$ and $C_{2g} = 51.6$ K). Indeed, the fits done for viscosity and translational diffusion data concerned different sucrose concentrations. The C_{1g} and C_{2g} values are therefore mean values which correspond to the sucrose−water system. Angell et al.[38] suggested that the "fragility", and then the C_{2g} coefficient, of carbohydrates could be influenced by the water content. It appears that, for the range of water content studied in the present work, at least, the variation of fragility was not significant. The modeling of diffusion data with expression 6 has a practical interest and should help the food industry to predict the evolution of changes in products as a function of the processing or storage temperature.

The diffusion values in the vicinity of the glass transition were not taken into account for the WLF predictions because in this range of temperatures the measured translational diffusion coefficients were truly higher than expected from eq 6. Indeed, at temperatures close to T_g, for the highest sucrose concentrations, viscosity and translational diffusion were decoupled and

TABLE 2: Values of the Apparent Activation Energy for the Diffusion of Fluorescein and for the Viscosity of the Sucrose Solutions: $-\ln(D)$ or $\ln(\eta) = -E_a/RT$

sucrose concentration (g/100 g)	activation energy (kJ mol⁻¹)	
	E'_{app} diffusion of fluorescein	E_{app} viscosity of the matrix
43.5	33 ± 2	35 ± 2.4
57.5	50 ± 2	48 ± 1.5
65.3	55 ± 3	70 ± 2.5
84.0	155 ± 9	175 ± 4[a]
90.0	59 ± 10	316 ± 16[a]

[a] The activation energy for the viscosity of the 84.5% and 90% sucrose solution was calculated from the WLF equation with $C_{1g} = -19.84$, $C_{2g} = 51.6$, $\eta_{T_g} = 1.6 \times 10^{12}$ Pa s.

evolved differently: whereas viscosity followed the WLF equation, translational motions did not.

To emphasize the decoupling effect, the measured translational diffusion coefficient values were fitted to an Arrhenius equation, and a precise analysis of the apparent activation energy for diffusion and viscosity was done in a temperature range (−15 to 20 °C) for different concentrations:

$$\ln \eta = -\frac{E_{app}}{RT}$$

$$\ln D_{trans} = \frac{E'_{app}}{RT} \tag{7}$$

with E_{app} and E'_{app}, the apparent activation energies for the viscosity and the diffusivity respectively, and R, the gas constant.

The apparent activation energy (E_{app}) for viscosity was calculated for three sucrose concentrations: 43.5%, 57.5%, and 65.3%. The results are reported in Table 2, where they are compared to those obtained for the measured translational diffusion coefficient values in the same temperature range (−15 to 20 °C). The activation energies for the 84.5% and 90% sucrose solutions were evaluated from the WLF equation (eq 3). The constants used for this calculation were $C_{1g} = -19.8$, $C_{2g} = 51.6$ K, and $\eta_{T_g} = 1.6 \times 10^{12}$ Pa s because this fit allowed a rational approximation of the viscosity at T_g, close to the value of 10^{12} Pa s, which is generally considered for η_{T_g}. The apparent activation energy increased as the ratio T_g/T increased, diffusivity or viscosity becoming more sensitive to the temperature as the system approached its glass transition temperature. The activation energy values for diffusion and viscosity were similar for sucrose concentrations up to 57.5%. In contrast, highly concentrated sucrose solutions exhibited a decoupling effect between diffusion and viscosity. English and Dole[39] had also compared the activation energy for these two processes:
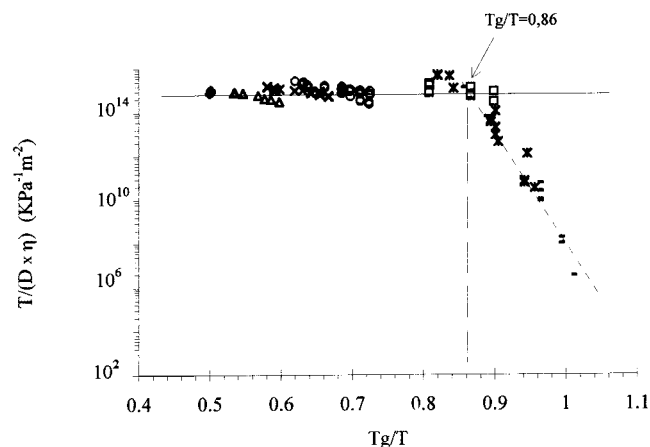
Figure 3. $T/(D\eta)$ as a function of the inverse temperature for supercooled sucrose solutions. Diffusion coefficients are experimental data ($\diamond$ for 30% sucrose, $\triangle$ 43.5%, $\times$ 57.5%, $\bigcirc$ 65.3%, $\square$ 84%, $*$ 87%, $-$ 90%) and viscosity values are predicted with the WLF equation. The solid line ($-$) is the plot of the SE relation, and the dashed line is a guide for the eye for sucrose concentrations of 87% and 90%.

viscosity and diffusion for a sucrose concentration range of 60%−72%. Our results converge with theirs: the higher the concentration, the more the activation energy for viscous flow deviates from that for diffusion.

Discussion

Our results show that the translational mobility of the small tracer becomes much larger than predicted by the WLF model; the diffusion coefficient has a weaker temperature dependence than expected from the shear viscosity, particularly at temperatures close to T_g. We considered that two steps have to be distinguished in the deviation between translational mobility and shear viscosity: the deviation emphasized by apparent activation energy values, becoming apparent for concentrations above ≈65% ($T_g/T \approx 0.65$), and the decoupling observed for $T_g/T \approx$ 0.86, amounting to a factor of 10^5 between the measured diffusion coefficient and the D_{T_g} predicted values. The first small deviation, observed for concentrations higher than about 65%, is not sufficient to substantiate a true decoupling between the two physical behaviors, but can simply be attributed to a change of the probe radius with decreasing water content. Figure 3 allowed us to check the validity of the SE relation: the plot of $T/D\eta$ (with η predicted by WLF) as a function of T_g/T should give a constant equal to $6\pi r/k_B$ if eq 6 could be applicable in the studied temperature range. For concentrations lower than 84.5%, there was just a small deviation from the calculated value for the constant ($6\pi r/k_B$); but for concentrations of 87% and 90%, the diffusion behavior was clearly different. In the literature, rotational diffusion coefficients were found to roughly follow the viscosity evolution in different systems such as *o*-terphenyl[10] or glycerol,[6] and the deviation which could be observed near T_g was also attributed to a possible small change of molecular shape or radius of the molecules in the highly viscous regime. This small deviation never exceeded a decade between the rotational diffusion calculated from the viscosity $D_{rot} = k_B T/8\pi r^3 \eta$ and the measured values; on the contrary, the translational diffusion coefficients showed a deviation of at least 2−5 decades with predictions from eq 6 in the vicinity of the glass transition:[8] such large decoupling could not be explained by a simple change in molecular shape. Indeed, similar enhancements of experimental translational diffusion coefficients, compared with the mobility predicted from viscosity

near T_g, have recently been observed in other glass-forming liquids. OTP,[9,10,19,22,29,30] tricresyl phosphate[22,30] (TCP), toluene, and trinaphthylbenzene[25,31] (TNB) were the most studied liquid glass formers. Both translational and rotational diffusions were studied for these systems. Whereas the rotational mobility was still in agreement with the evolution of the shear viscosity as a function of temperature, the translational diffusion showed a decoupling effect for these systems. The enhancement of translational diffusion coefficients near T_g was explained by several theories based on the decoupling either between viscosity and translational mobility[9,22,29,40] or between rotational and translational diffusion coefficients.[31,41] Some models,[29,31,41] which are based on some physical or energetic spatial heterogeneities, assume that the SE relation is valid locally or temporarily in mobile domains which allow fast translational motions. These models give a plausible explanation for the decoupling between rotational and translational diffusion coefficients, but the breakdown from the SE relation of translational diffusion and viscosity at a given temperature is not clearly introduced. Indeed, Figure 3 shows that the mechanism of translational motions changes from the SE behavior to another one for the highly concentrated solutions, at a critical temperature which is close to $1.2T_g$. Rössler[19,21,22,42] reported similar observations for the diffusion of tracers in various liquids (OTP, TNB, TCP) and related this critical temperature to the temperature T_c introduced by the mode-coupling theory.[19,20] The breakdown of the SE relation below T_c was related to changes in dynamical properties revealed by the separation of the α and β processes. However, the mode-coupling theory, which predicts successfully the temperature dependence of viscosity above T_c with the power law (eq 4), does not result in satisfactory predictions for mechanical properties between T_c and T_g and does not provide any quantitative prediction for translational motions in that temperature range. To describe on a molecular basis what happens between T_c and T_g, a model of hierarchically correlated molecular motions has been proposed.[43,44] The model predicts a temperature $T_{\alpha\beta}$ for which the α and β relaxation processes should merge and which is approximately $1.1-1.2T_g$.[45] The agreement between our experimental critical temperature ($T_g/T = 0.86$) (Figure 3) and the $T_{\alpha\beta}$ predicted by this model allows us to think that the tracer translational mobility should be facilitated by local movements of the matrix. Our translational diffusion data will be discussed in terms of the model proposed by Perez et al.[45] in a further paper together with supplementary experimental results of mechanical spectroscopy in order to test the validity of the hypothesis.

It must be stressed that most, if not all, translational diffusion data discussed before were obtained using a host molecule (the tracer) in a guest amorphous matrix, with either the forced Rayleigh scattering or FRAP techniques. The motion of the probe was found to decouple from the viscosity of the matrix, although the tracer was chosen for its size, comparable to the size of the molecule composing the matrix (ACR or TTI in OTP[10,16,26,37] or fluorescein in sucrose). The translational motion of a host molecule may not be able to follow the viscosity of the matrix if this molecule does not really belong to the medium and may move following its own way when the viscosity increases. A measurement of the sucrose self-diffusion should allow one to check the validity of the SE relation in the vicinity of the glass transition, better than the study of tracer motions in a guest matrix. The translational diffusion of a polymer labeled with a dye probe,[25] in a polymeric matrix, takes more consideration of the self-diffusion in the system; in this case, diffusion and viscosity are found to be more in agreement with

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the VTF model.[46] The polymer tracer is probably more linked to the matrix and emphasizes the behavior of the whole system.

Conclusion

Translational diffusivity of a tracer in supercooled concentrated sucrose solutions was shown to follow a model derived from the SE relation between diffusivity and viscosity and the WLF equation describing the temperature dependence of viscosity. This was true for temperatures above about $1.2T_g$. In the temperature range $1.2T_g$ to T_g, on the contrary, the translational diffusion coefficients of the tracer showed a weaker temperature dependence than the shear viscosity. An important feature of these results, similar to others obtained in apolar organic liquids, is that they were obtained in aqueous solutions where the predominant intermolecular interactions were H bonds. The decoupling temperature, together with the Arrhenius-like behavior of the molecular mobility observed below this temperature lead us to imagine a relationship with a β relaxation process. This hypothesis has to be discussed in connection with mechanical spectroscopy experiments, allowing the study of the β relaxation. Rotational diffusion measurements will also be used to discuss further the validity of the SE relation near T_g.

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