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# On The Use of The WLF Model in Polymers and Foods

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**ABSTRACT:** The validity of the WLF model with fixed "universal" coefficients was tested against that of the model original form with variable coefficients using published coefficients of polymers and amorphous sugars crystallization and viscosity data. The disagreement between the two versions of the model is particularly large at temperature ranges starting about 20 to 30°K above the glass transition or reference temperature, excluding the former from being a model of general applicability. Because the WLF model mathematical structure entails the existence of an almost linear region near the reference temperature, establishment of its validity as a kinetic model and meaningful determination of its constants requires data spread over an extended temperature range, especially when the experimental results have a scatter.

**KEY WORDS:** kinetics, viscosity, sugars, glass transition.

## I. INTRODUCTION

The concept that glass transition is a key factor in regulating the physical, chemical, and biological stability of foods has recently gained prominence and wide acceptance.[1,2] The phenomenon of glass transition itself has received considerable attention because of its pertinence to the flowability and mechanical behavior of amorphous polymers.[3,4] But it was also investigated in other types of materials, including sugars.[5,6] Models that relate viscosity to temperature are an essential tool in any quantitative analysis of the phenomenon and its impact on the physical properties of materials. In fact, there are several such models.[3,4] But, apart from the Arrhenius equation, the one most popular, at least in the more recent food literature, is the one known as the WLF model named after its proposers, Williams, Landel, and Ferry. Its original form is[7]

$$\log_{10} a_T = -C_1 (T-Ts)/(C_2+T-T_s) \quad (1)$$

where $a_T$ is the ratio between viscosity at a temperature T, and the viscosity at a reference temperature $T_s$, i.e.,

$$a_T = \eta(T)/\eta(T_s) \quad (2)$$

and $C_1$ and $C_2$ constants.

It ought to be added that the model is not limited to viscosity only. It can also accommodate other mechanical relaxation or rate parameters such as tensile strength or strain[4] and compliance.[3] Although most of the following discussion will address $a_T$ in terms of a viscosity ratio, it is just as pertinent to other physical parameters to which the model is applied.

It was shown that Equation 1 holds very well especially when the reference temperature, $T_s$, which can be selected arbitrarily, is at least about 50°C above the glass transition temperature, $T_g$. (The general applicability of Equation 1 is also limited to temperatures above $T_g$, but this should not concern us here.) When the magnitude of

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Equation 1 constants, of various polymers, with the reference temperature 50°K above $T_g$ was averaged the mean values of $C_1$ and $C_2$ were 8.86 (dimensionless) and 101.6 (°K), respectively. Thus when the reference temperature was shifted by 50°K (see below), the glass transition temperature, $T_g$, became the reference temperature and Equation 1 was transformed into the now familiar form

$$\log_{10} a_T = -17.44\,(T - T_g)/(51.6 + T - T_g) \quad (3)$$

However, the original authors of the WLF model advised *against* the use of Equation 3 because of the "uncertainties in specifying $T_g$ and difficulty of experimental measurements near $T_g$."[7] This warning is repeated by Ferry,[3] who stated that because the "actual variation form one polymer to another is too great" Equation 3 can only be used "as a last resort in the absence of other specific data."

Furthermore, one can argue that since the constants of Equation 3 were derived by averaging data of different types of polymers, the equation need not be applicable to any particular system. (In a variety of polymers for which Equation 1 was applied with $T_g$ as a reference point[3] ($T_s = T_g$), see below, the magnitude of $C_1$ varied between 13.7 and 34 and that of $C_2$ between 24 and 80°K.) Even in the frequently cited paper on the temperature-viscosity relationships in sugar solutions by Soesanto and Williams[5] where a successful use of Equation 3 is reported, the authors themselves admit that "While the successful curve fit does not provide absolute verification of $C_1$ and $C_2$ values — since *Tg and* $\eta_g$ *were optimized to approach such success* — it does lend credence to them. *Very similar values* were obtained when different reference temperatures were used (60 and 80°C rather than Tg) in Equation 3 and the alternate pair $C_1'$, $C_2'$ translated to $C_1$,$C_2$ by shifting these results to Tg. Trials with other values for the $C_1$,$C_2$ pair failed to give curve fits superior to that seen in (the) figure."

In Equation 1 in contrast, $T_g$ and $\eta_g$, which are objective and measurable material properties, need no "optimization", but the constants $C_1$ and $C_2$ are allowed to vary. Consequently, the magnitude of $C_1$ and $C_2$ must depend not only on the material but also on the selected reference temperature, $T_s$. A food example is the temperature dependency of the elongational viscosity of melted process American cheese reported by Campanella et al.[8] (Figure 1). The fit of Equation 1 in the temperature range of 35 to 60°C was almost perfect and practically the same with the selected reference temperature, $T_s$, being either 36 or 45°C. The corresponding magnitudes of the constants $C_1$ and $C_2$, however, were 1.7 and 21°K in the first case and 1.1 and 27°K in the second.

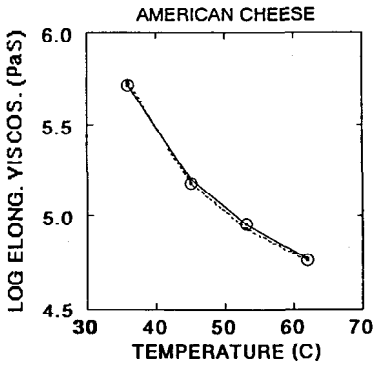


**FIGURE 1.** Demonstration of the fit of the WLF model (Equation 1) to elongational viscosity data of process American cheese. Open circles are the experimental data, solid line is the model fit with $T_s$ = 36°C, dashed is line with $T_s$ = 45°C. (From Campanella et al., *J. Food Sci.*, 52, 1249, 1987. With permission.)

Because the models expressed by Equations 1 and 3 are not mathematically identical, the question arises whether they can still be used interchangeably and how they compare *quantitatively* when applied to the same set of experimental viscosity data. The objectives of this work are to examine the agreement between the model's two version using published constants of polymers and reported viscosity and crystallization data on amorphous sugars crystallization results, and to demonstrate that a valid comparison between the model's two versions can be made even when viscosity data at or near the glass transition temperature itself are unavailable. However, the discussion will only deal with the mathematical compatibility of Equations 1 and 3 and its implications. It will not address the issue of how the WLF equation compares with alternative mathematical expressions as a kinetic model of physicochemical changes in foods.

## II. METHODS OF COMPARISON

The degree of compatibility between Equations 1 and 3 can be assessed in three ways. In Ferry's book on the viscoelastic properties of polymers,[3] there is a table listing the constants $C_1$ and $C_2$ of a variety of polymers. For some of them the reference temperature is the glass transition temperature itself that is $T_s = T_g$. In such case one can generate two curves of $\log_{10} a_T$ vs. T one with the reported $C_1$ and $C_2$ and the other with $C_1 = 17.44$ and $C_2 = 51.6$ K. (The traditional $\log_{10} a_T$ vs. $T-T_g$ or $T-T_s$ plot is not needed here since both relationships have the same reference temperature.) If the two models are interchangeable, the two curves will coincide or at least overlap over a considerable temperature range above $T_g$. In case they do not coincide, the gap between the two curves provides a measure of the degree of incompatibility between the two models for the particular polymer.

For most of the polymers though the reported reference temperature $T_s$ is higher than the glass transition temperature $T_g$, which excludes the former method. However, one of the mathematical properties of Equation 1 is that it enables simple calculation of the constants when the reference temperature is shifted. It can be shown[3,7] that if the reference temperature $T_s$ is shifted to a lower temperature $T_s'$ ($T_s' = T_s - \delta$ where $\delta$ is the shift in °K) then the new constants, $C_1'$ and $C_2'$ are

$$\text{and } C_1' = C_1C_2/(C_2 - \delta) \qquad (4)$$

and

$$C_2' = C_2 - \delta \qquad (5)$$

The original Equation 1 is now transformed into

$$\log_{10} [\eta(T)/\eta(T_s'] = -C_1C_2(T-T_s')/[(C_2-\delta) \times (C_2-\delta+T-T_s')] \qquad (6)$$

If the new reference temperature is $T_g$, then for every pair of constant $C_1$ and $C_2$ Equation 6 becomes

$$\log_{10} a_T = \log_{10} (\eta(T)/\eta(T_g)] = -C_1C_2 (T-T_g)/[(C_2-\delta) (C_2-\delta+T-T_g)] \qquad (7)$$

Equation 7 can be used to generate a $\log_{10} a_T$ vs. T plot originating in $T_g$ that can be directly compared with a corresponding plot produced using Equation 3 with the same value of $T_g$ inserted into the two equations.

The same method can also be applied in reverse, that is, using Equation 3 as the starting model and shifting up the reference temperature from $T_g$ to a new reference temperature $T_s$. This will give

$$C_1 = 17.44 \times 51.6/(51.6 + \delta) \qquad (8)$$

and

$$C_2 = 51.6 + \delta \qquad (9)$$

and finally:

$$\log_{10} a_T = \log_{10}[\eta(T)/\eta(T_s)] = -899.9 (T - T_s)/[(51.6 + \delta) (51.6 + \delta + T - T_s)] \qquad (10)$$

This option is particularly attractive in systems where $\eta(T_g)$ is unknown or cannot be reliably measured, and where $C_1$ and $C_2$ are unknown and there is doubt whether the WLF model itself is at all applicable (see later). In such cases a $\log_{10} a_T$ vs. T relationship can be created on the basis of the reported (or an original set) experimental results, with a related reference temperature, $T_s$, within or at the end of the experimental range. The resulting plots can then be directly compared with a corresponding plot generated using Equation 10 with the same reference temperature.

## III. COMPARISON BETWEEN THE WLF MODEL'S TWO VERSIONS

### A. Comparison of Equations 1 and 3 for Polymers When $T_s = T_g$

Examples of generated $\log_{10} a_T$ vs. T plots using Equation 1 (open circles) (constants listed in Table 1) and Equation 3 (solid lines) are shown in Figures 2 and 3. The figures clearly demonstrate that the difference in the constants' magnitude, 14.5 to 16.2 vs. 17.44 of $C_1$ and 24 vs. 51.6°K of $C_2$, was sufficient to introduce a dis-

**TABLE 1**
**Reported and Recalculated WLF Equation Constants of Various Polymers[a]**

| Polymer | $T_s$ (°K) | $C_1$ (−) | $C_2$ (°K) | $T_g$ (°K) | Of curves shifted to $T_s = T_g$[b] $\delta$ (°K) | $C_1'$ (−) | $C_2'$ (°K) |
|---|---|---|---|---|---|---|---|
| Polyacetaldehyde | 243 | 14.5 | 24 | 243 | 0 | 14.5[c] | 24[c] |
| Polypropyleneoxide | 198 | 16.2 | 24 | 198 | 0 | 16.2[c] | 24[c] |
| Polyisobutylene | 298 | 8.61 | 200.4 | 205 | 93 | 16.0 | 107.4 |
| Polyvinylacetate | 349 | 8.86 | 101.6 | 305 | 44 | 15.6 | 57.6 |
| Polystyrene | 373 | 12.7 | 49.8 | 370 | 3 | 13.5 | 46.8 |
| Polybutadiene cis-trans (rubber) | 298 | 3.64 | 186.5 | 172 | 126 | 11.2 | 60.5 |
| Polyurethane (rubber) | 283 | 8.86 | 101.6 | 238 | 45 | 15.9 | 56.6 |

[a] Constant from Reference 3.
[b] Transformed using Equations 4 and 5.
[c] By definition.

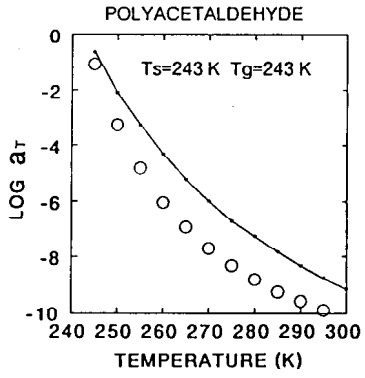


**FIGURE 2.** Generated WLF plots of polyacetaldehyde using Equation 1 (open circles) and Equation 3 (solid line). Equation 1 constants[3] are listed in Table 1. (Note that $T_s = T_g$.)

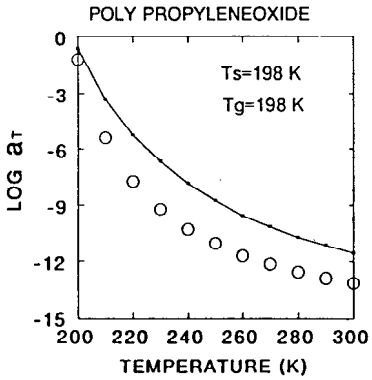


**FIGURE 3.** Generated WLF plots of polypropyleneoxide using Equation 1 (open circles) and Equation 3 (solid line). Equation 1 constants[3] are listed in Table 1. (Note that $T_s = T_g$.)

crepancy of about two orders of magnitude in the values of the respective viscosity ratio at temperatures about 20°K above $T_g$. Or, in other words, for at least the two polymers, polyacetaldehyde and polypropylene oxide, Equations 1 and 3 cannot be used interchangeably except for temperatures that are only a few degrees above $T_g$.

## B. Comparison of Equations 1 and 3 with Shifted Curves of Polymers

Examples of generated $\log_{10} a_T$ vs. T plots of five polymers, three "general" and two rubbers,[3] are shown in Figures 4 to 8. They were generated using Equation 3 (solid lines) and Equation 7 (open circles) with the constants listed in Table 1. The figures show that the discrepancy between the two models is larger in polyisobutylene and polybutadiene (Figures 4 and 7) than in the other three polymers, i.e., polyvinylacetate, polystyrene, and polyurethane (Figures 5, 6, and 8, respectively). Since the figures are not drawn to the same scale the magnitude of the discrepancies can be better judged when determined at let's say 20 and 50°K above $T_g$ as shown in Table 2. The table demonstrates that when in those polymers where certain agreement between

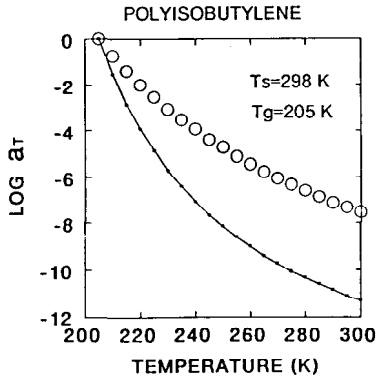


**FIGURE 4.** Generated WLF plots of polyisobutylene using Equation 7 (open circles) and Equation 3 (solid line). Equation 7 constants[3] are listed in Table 1.

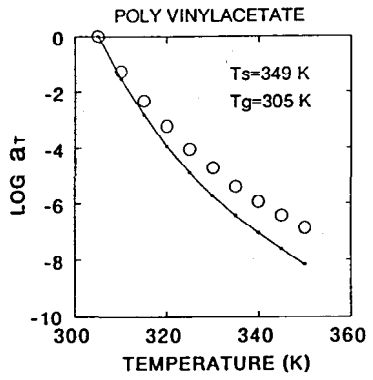


**FIGURE 5.** Generated WLF plots of polyvinylacetate using Equation 7 (open circles) and Equation 3 (solid line). Equation 7 constants[3] are listed in Table 1.

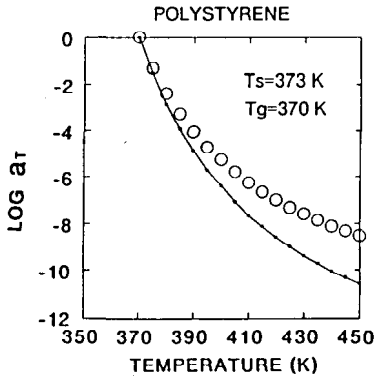


**FIGURE 6.** Generated WLF plots of polystyrene using Equation 7 (open circles) and Equation 3 (solid line). Equation 7 constants[3] are listed in Table 1.

the two versions of the WLF model could be contemplated it would be still unsafe to use Equation 3 for temperatures about 50°K above the glass transition temperature. The reverse is also

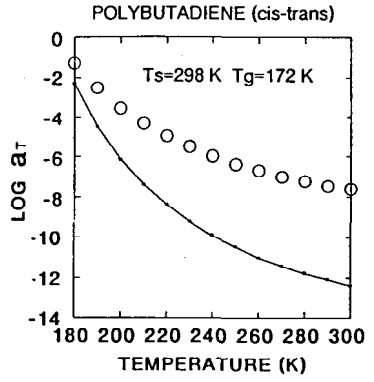


**FIGURE 7.** Generated WLF plots of polybutadiene using Equation 7 (open circles) and Equation 3 (solid line). Equation 7 constants[3] are listed in Table 1.

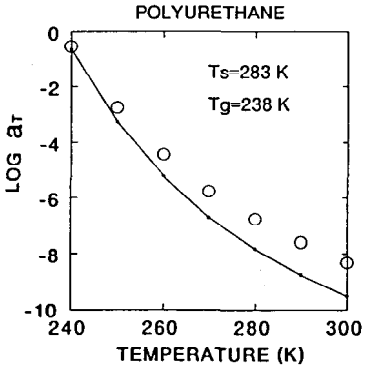


**FIGURE 8.** Generated WLF plots of polyurethane using Equation 7 (open circles) and Equation 3 (solid line). Equation 7 constants[3] are listed in Table 1.

true here (see below), that is extrapolated data from such a temperature range, i.e., about or more than 50°K above $T_g$, cannot be used to predict the system's behavior at or near $T_g$ employing Equation 3 as a model. In principle, the described procedure could also be used to verify the appropriateness of Equation 3 to the viscosity of sugar solutions reported by Soesanto and Williams.[5] Unfortunately, though, the magnitudes of the constants $C_1$ and $C_2$ obtained when the reference temperature was 60 or 80°C are not reported in their paper.

## C. Crystallization of Amorphous Sugars

As previously mentioned, the applicability of the WLF model is not restricted to viscosity ratio. In the case of amorphous sugars, the time it takes for the material to crystallize can be considered

**TABLE 2**
**Comparison of the Degree of Disagreement between Equations 3 and 1 in Various Polymers[a]**

| Material | Approximate gap ($log_{10}$ units) $T = T_g + 20°K$ | $T = T_g + 50°K$ |
|---|---|---|
| Polyacetaldehyde[b] | + 1.7 | + 1.2 |
| Polypropylene oxide[b] | + 2.5 | + 2.3 |
| Polyisobutylene[c] | − 2.3 | − 3.4 |
| Polyvinylacetate[c] | − 0.8 | − 1.3 |
| Polystyrene[c] | − 0.8 | − 1.6 |
| Polybutadiene cistrans[c] | − 1.9 | − 3.5 |
| Polyurethane[c] | − 0.5 | − 1.0 |

[a] Equation 1 constants $T_g$ and $T_s$, listed in Table 1, are from Reference 3.
[b] $T_s = T_g$ (Figures 2 and 3).
[c] $Log_{10}\ a_T$ vs. T plots shifted to $T_g$ using Equation 7 (Figures 4 to 8).

as an index of internal molecular mobility and treated with the WLF model.[9] Application of Equation 10 to published crystallization data of dry amorphous lactose and sucrose are shown in Table 3 and Figures 9 and 10. Since in the original publication the glass transition was specified in terms of $T_{g1}$ and $T_{g2}$ representing the onset and termination of the transition, respectively, the analysis includes both. As shown in Figure 9 the discrepancy between the predictions of Equation 3 and the actual data is quite large irrespective of how $T_g$ is defined. There is a somewhat better agreement in the case of the amorphous sucrose, Figure 10, but the results scatter does not permit a decisive establishment of this as a fact. In both cases as in the polymers, the disagreement between the two model versions grows as the temperature increases.

One can also observe that the $log_{10}\ a_T$ vs. T plots of both sugars could be equally represented by a straight line. (Linear regression of the data yielded $r = -0.994$ for the lactose and $r = -0.934$ for the sucrose.) This is not surprising because the mathematical structure of the WLF model entails the existence of a nearly linear relationship between $log_{10}\ a_T$ and T around the ref-

**TABLE 3**
**Recalculated WLF Model Constants Using Equation 3 and Crystallization Data of Amorphous Sugars**

| Sugar | $T_{g1}$ and $T_{g2}$ (°K) | $T_s$ (°K) | δ (°K) | Calculated Equation 1 coefficients[a] $C_1$ (−) | $C_2$ (°K) |
|---|---|---|---|---|---|
| Amorphous lactose | 374 | 408 | 34 | 10.5 | 85.6 |
| (dry) | 382 | 408 | 26 | 11.6 | 77.6 |
| Amorphous sucrose | 329 | 353 | 24 | 11.9 | 75.6 |
| (dry) | 342 | 353 | 11 | 14.4 | 62.6 |

[a] $C_1$ and $C_2$ were calculated using Equations 8 and 9. Note the discrepancy between the predictions of the model and the actual data shown in Figures 9 and 10.

Data from Reference 9.

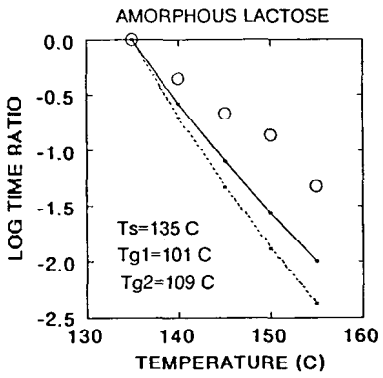


**FIGURE 9.** Comparison of experimental crystallization data of amorphous lactose (open circles) and the predictions of Equation 3. (Solid line $T_{g1}$ = 101°C, dashed line $T_{g2}$ = 109°C). (From Roos, Y. and Karel, M., *J. Food Sci.*, 56, 38, 1991. With permission.)

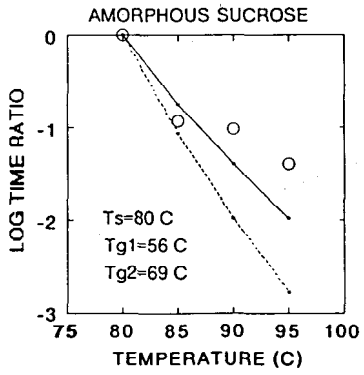


**FIGURE 10.** Comparison of experimental crystallization data of amorphous sucrose (open circles) and the predictions of Equation 3. (Solid line $T_{g1}$ = 56°C, dashed line $T_{g2}$ = 69°C.) (From Roos, Y. and Karel, M., *J. Food Sci.*, 56, 38, 1991. With permission.)

erence temperature. When $T \simeq T_s$, $T - T_s \ll C_2$ and Equation 1 degenerates into:

$$\log_{10} a_T \simeq -C_1 (T - T_s)/C_2 = C_1 T_s/C_2 - (C_1/C_2)T \quad (11)$$

Thus, if the experimental results have even a small scatter, it will be very difficult to calculate the WLF model constants correctly when the data base is restricted to a small temperature range. Or, in other words, establishment of the WLF model validity as a kinetic model and reliable calculation of its constants can only be done if the experimental temperature range is sufficiently wide for the curvature of the $\log_{10} a_T$ vs. T relationship to be fully expressed.

## D. The Viscosity of Fructose

Experimental viscosity-temperature relationship of fructose in the range of about 25 to 80°C above the glass transition temperature was recently reported by Ollett and Parker.[6] Their data redrawn in the form of a WLF plot with 40°C as the reference temperature are presented in Figure 11. The figure shows the fit of Equation 3 with three different published values of $T_g$ that are also reported in the work (solid lines). The plots show a remarkable agreement between the experimental data and Equation 3 *if* the glass transition temperature is 13°C (286°K). There is a somewhat lesser agreement if $T_g$ = 7°C (280°K) and a substantial discrepancy if $T_g$ = 30°C (303°K). However, the same experimental data can also be fitted by Equation 1, see dashed line in Figure 11, in which case $C_1$ = 12.7 and $C_2$ = 88.3°K. These values can be used to shift the reference temperature to the different transition temperatures employing Equation 7, and compare the arrived at magnitudes of the calculated viscosities with those using Equation 3 with its fixed "universal" coefficients ($C_1$ = 17.44 and $C_2$ = 51.6°K). The results of this comparison are given in Table 4. It shows that when the WLF model is used for extrapolation, there is a considerable gap between the viscosity values calculated by its two versions. Even in the case where both versions had a comparable fit in the limited experimental temperature range ($T_g$ = 13°C), the extrapolated viscosities at the glass transition temperature differed by a factor of about two.

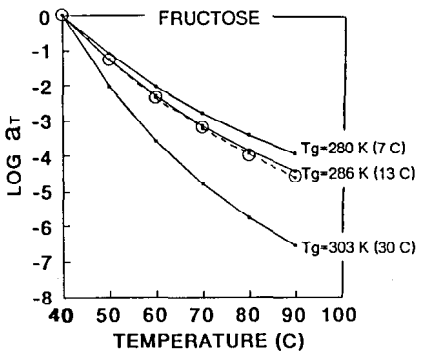


**FIGURE 11.** WLF plots of fructose with $T_s$ = 40°C. Open circles are experimental data. Solid lines are the predictions of Equation 3 with three published values of $T_g$. Dashed line is the fit of Equation 1. (From Ollett, A. L. and Parker, R., *J. Texture Stud.*, 21, 355, 1990. With permission.)

**TABLE 4**
**Glass Transition Viscosity of Fructose Calculated by Extrapolation of the Two Versions of the WLF Model**

| $T_g$ (°C) | Viscosity at $T_g$ calculated by extrapolation (PaS) Equation 1[a] | Equation 3 | Approximate ratio |
|---|---|---|---|
| 7 | $1.7 \times 10^{13}$ | $2.8 \times 10^{12}$ | 6:1 |
| 13 | $1.8 \times 10^{11}$ | $4.4 \times 10^{11}$ | 1:2.5 |
| 30 | $1.9 \times 10^{7}$ | $3.0 \times 10^{6}$ | 1:16 |

[a] Calculated with $C_1 = 12.7$, $C_2 = 88.3$°K, $T_s = 40$°C and $\eta(40°C) = 5.8 \times 10^5$ Pa.s (an experimentally determined value).

Moreover, $T_g$ as previously stated is a physical property that can and should be determined independently, by DSC, for example, and not by extrapolation of the WLF plot to a given viscosity using either version of the WLF model. Table 4 also demonstrates the sensitivity of the magnitude of the extrapolated viscosity to that of the selected $T_g$. If indeed $T_g$ of fructose is between 7 and 30°C as reported then its viscosity according to the WLF model should be between an upper and lower limit differing by about four orders of magnitude if Equation 3 is used and about five orders of magnitude if Equation 1 is used. Needless to say it would be much safer in such a case to try to estimate the viscosity through a direct physical method rather than by extrapolation using the WLF or any other model.

## IV. CONCLUSIONS

The WLF equation with fixed coefficients (Equation 3) cannot be assumed as a generally valid model. As demonstrated in polymers and amorphous sugars, its use may lead to a considerable error in the viscosity magnitude, especially if the pertinent temperature range starts about 20 to 30°K or more above the glass transition temperature, or when employed, through extrapolation, to calculate the viscosity at $T_g$.

The validity of the WLF model with fixed or variable coefficients can be tested for temperatures near $T_g$ even when the viscosity (or an equivalent physical property) at and around $T_g$ is unknown. Owing to the mathematical properties of the model this can be done through shifting the $\log_{10}$ vs. T plot to the desired temperature range with a corresponding transformation of the model's constants. The WLF model entails an almost linear region near the reference temperature. Consequently, establishment of its validity as a kinetic model and determination of its constants, especially when the experimental data have a scatter, requires results over a large temperature range. It is recommended that the WLF model, where applicable in light of physicochemical considerations, be only used in the original form (Equation 1), that is, with the reference temperature within the experimental range and the coefficients variable.

## ACKNOWLEDGMENT

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