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Non-Arrhenius and non-WLF kinetics in food systems

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Abstract: The classic Arrhenius and WLF equations are commonly used to describe rate–temperature relations in food and biological systems. However, they are not unique models and, because of their mathematical structure, give equal weight to rate deviations at the low- and high-temperature regions. This makes them particularly useful for systems where what happens at low temperatures is of interest, as in spoilage of foods during storage, or where the effect is indeed exponential over a large temperature range, as in the case of viscosity. There are systems, however, whose activity is only noticeable above a certain temperature level. A notable example is microbial inactivation, for which these two classical models must be inadequate simply because cells and spores are not destroyed at ambient temperature. For such systems a model that identifies the temperature level at which the rate becomes significant is required. Such an alternative model is $Y=\ln\{1+\exp[c(T-T_c)]\}^m$, where Y is the rate parameter in question (eg a reaction rate constant), T_c is the marker of the temperature range where the changes accelerate, and c and m are constants. (When $m=1$, Y at $T \gg T_c$ is linear. When $m \neq 1$, m is a measure of the curvature of Y at $T \gg T_c$.) This model has at least a comparable fit to published rate–temperature relationships of browning and microbial inactivation as well as viscosity–temperature data previously described by the Arrhenius or WLF equation. This alternative log logistic model is not based on the assumption that there is a universal analogy between totally unrelated systems and simple chemical reactions, which is explicitly assumed when the Arrhenius equation is used, and it has no special reference temperature, as in the WLF equation, whose physical significance is not always clear. It is solely based on the actual behaviour of the examined system and not on any preconceived kinetics.

Keywords: kinetics; temperature; oxidation; browning; microbial inactivation; viscosity; energy of activation

INTRODUCTION

Most, if not all, foods are chemically or biologically active. Consequently, they undergo changes, the rate of which is temperature-dependent. The changes themselves can be undesirable, browning or lipid oxidation for example, or desirable like the increase in the mortality rate of micro-organisms when exposed to lethal temperatures. They can also be reversible, as in the case of a viscosity decrease or increase, or irreversible like most of those caused by chemical reactions. Not surprisingly, the rate–temperature relationship in food systems has been a central topic in food research and there are hundreds or perhaps even thousands of publications that deal with the issue in one form or another.

The most common mathematical model to describe the effect of temperature on the rate of chemical and biochemical reactions has been the Arrhenius equation. Its application has been extended to the effect of temperature on viscosity (see eg Ref 1) and microbial inactivation during heat pasteurisation and sterilisation (see eg Ref 2). The model is usually expressed in the form

$$k = k_0 \exp\left[\frac{E}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right] \tag{1}$$

or

$$\ln\left(\frac{k}{k_0}\right) = \frac{E}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right) \tag{2}$$

where k is the reaction rate at a temperature T in degrees K, k_0 is the rate constant at a reference temperature T_0, E is the 'energy of activation' in J mol^{-1} or cal mol^{-1} and R is the gas constant expressed in the corresponding units. In rheology the Newtonian viscosity μ or apparent viscosity μ_a replaces the rate constants k and k_0. One of the most obvious advantages of the Arrhenius model is that in systems where it applies, knowing the values of k or μ at any two temperatures is

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sufficient to calculate E/R. Once calculated, eqn (2) can be used to estimate the magnitude of k or μ at any other temperature in the pertinent range. The Arrhenius model entails that the plot of $\ln k$ (or $\ln\mu$) *versus* $1/T$ is a straight line with a slope E/R from which the 'energy of activation' is extracted. It was originally developed for simple chemical reactions where the rate constant k is clearly defined. However, linear $\ln k$ *versus* $1/T$ plots have been found quite frequently in other and more complex systems, hence the widespread use of this model.

There are systems, however, for which the Arrhenius model is clearly inadequate. This is revealed by a noticeable curvature in their $\ln k$ *versus* $1/T$ plots. The effect of temperature on the kinetics of such systems has been described by a variety of alternative models. Among them, the one that has become very popular in food research is the WLF equation. It was originally proposed for quantifying the effect of temperature on the viscosity of polymers above their 'glass transition temperature' T_g. Its general form is[3]

$$\log_{10}\left(\frac{\mu}{\mu_s}\right) = -\frac{C_1(T - T_s)}{C_2 + (T - T_s)} \tag{3}$$

where μ_s is the viscosity at a reference temperature T_s, and C_1 and C_2 are constants. Its most familiar form and the one most commonly used in the food literature is

$$\log_{10}\left(\frac{\mu}{\mu_g}\right) = -\frac{C_1'(T - T_g)}{C_2' + (T - T_g)} \tag{4}$$

where μ_g is the viscosity at the 'glass transition temperature' T_g, and C_1' and C_2' are constants whose values are different from those of C_1 and C_2 in eqn (3); or, when applied to other rate or 'relaxation' parameters,

$$\log_{10}(a_T) = -\frac{C_1'(T - T_g)}{C_2' + (T - T_g)} \tag{5}$$

where a_T is the ratio between the magnitudes of the parameter in question at temperatures T and T_g respectively. The WLF equation is a 'flexible' mathematical model. It can be shown that it will have almost the same fit with any reference temperature in the pertinent temperature range, although its constants will vary accordingly (see below). In foods this model has been used to describe a variety of systems. The shear viscosity of melted sugars,[4] oxidation and crystallisation rates[5,6] and the heat inactivation of bacterial spores[7] are a few examples. As late as the mid-1990s some authors have continued to use eqn (4) with $C_1' = 17.44$ and $C_2' = 51.6\,\mathrm{K}$, the so-called 'universal constants' (see eg Ref 8). These are mean values of an arbitrary number of synthetic polymers[3] and are useless for food (as well as for polymer) applications.[9,10] Almost invariably, when a 'successful application' of this model has been reported (see eg Ref 11), the authors have 'adjusted' the values of μ_g and T_g to fit the model instead of determining them experimentally (which in most cases is an impossible task—see below.)

THE PROBLEMS WITH THE APPLICATION OF THE ARRHENIUS AND WLF MODELS TO FOOD SYSTEMS

Let us assume that a chemical reaction, oxidation or browning for example, or the inactivation of an enzyme, microbial cells or spores, indeed follows first-order kinetics and that the rate constant k can be determined unambiguously. In reality this need not be the case, and expressing the rate in terms of a single time-independent constant is not possible. Since the focus of this discussion is the mathematical properties of models rather than the specific properties of the systems themselves, this issue will not be addressed despite its obvious implications. The same applies to viscosity or its reciprocal, flowability. Here too we will assume that it can be expressed or represented by a single temperature-dependent parameter. In reality the viscosity of complex foods is expected to be not only shear rate-dependent but also influenced by the mechanical history of the tested sample. Again, however, since we will only deal with the mathematical aspects of the models, these aspects will not concern us here. For the following discussion we will consider any rate constant k or viscosity μ as a valid representative of the behaviour of the corresponding system.

The Arrhenius equation

It is an empirical fact that in many systems at *a certain characteristic temperature range* the plot of $\ln k$ *versus* $1/T$ is a straight line or an approximately straight line as judged by statistical criteria. As long as this is acknowledged and the model is expressed in the form

$$Y = A\exp -\left(\frac{B}{T}\right) \tag{6}$$

or

$$\ln\left(\frac{Y_1}{Y_2}\right) = B\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{7}$$

where Y is the rate constant k or viscosity μ, and B is an adjustable parameter, everything is fine. A conceptual problem arises when the constant B, or E/R in the original model formulation, is used to calculate the so-called 'energy of activation'. For example, it is not at all clear what a kg mol of orange juice concentrate or of *Clostridium botulinum* spores means. Thus eliminating the 'energy of activation' and gas constant from the equation and expressing B in degrees K (Occam's razor) would be more natural. The magnitude of B, the slope of the $\ln Y$ *versus* $1/T$ relationship, would remain a measure of the temperature effect, which could be used to compare different systems or to calculate intermediate values of Y by interpolation. Moreover, in many cases, particularly in food microbiology, the magnitude of the 'energy of activation' is

determined by linear regression of experimental ln$k$ *versus* $1/T$ data. This gives an inappropriate weight or influence to the small inactivation rates at low temperatures, where the destructive effect is marginal, at the expense of the inactivation rates at high temperatures, where much of the process takes place on a time scale that can be shorter by one or more orders of magnitude. One can also surmise—consistently with the general concept of the existence of an energy barrier—that microbial and enzymatic inactivation starts in earnest *only* after a certain temperature range is reached. In such a case, identification of this temperature range would be most useful. Also, while Arrhenius kinetics implies that the ln$Y$ *versus* $1/T$ relationship is linear, the opposite need not be generally true. That the ln$k$ *versus* $1/T$ plot's slope provides the 'energy of activation' needs to be confirmed by an *independent assay*—something which has been missing in most if not all of the food publications where the use of the Arrhenius model is reported. It is quite possible (see below) that the Arrhenius model is not unique, in which case alternative interpretations of the ln$Y$ *versus* $1/T$ relationship would be equally plausible.

The WLF model

A 'WLF kinetics' has been proposed for systems where the ln$Y$ *versus* T plot is clearly non-linear.[12] As already mentioned, in most of the food publications where the use of the model is reported, it was presented in the form of eqn (4) or (5), ie with T_g as the reference temperature. There are three serious problems with this approach which are common to both synthetic polymers and foods.

1. Viscosity measurements in the glass transition region are extremely difficult if not impossible to perform.[3,13]
2. T_g is an ill-defined temperature. This is because the transition can take place over a temperature range of tens of °C,[14] which cannot be characterised by a single temperature. Also, the result of a 'T_g determination' strongly depends on the method chosen and on the rate at which the test is performed. This renders the commonly reported $T-T_g$ a dubious variable, especially for processes that take place at and around the transition temperature range.
3. In the transition region the concavity of the loga_T *versus* T relationship can be opposite to that predicted by the WLF model (see eg Refs 15 and 16).

It can be added that one of the most common definitions of T_g is the 'temperature where the material's viscosity reaches a level somewhere between 10^{13} and 10^{18} Pa s'. (The actual value varies among different literature sources.) Needless to say, these viscosities have rarely if ever been measured directly. Consequently, determination of T_g through extrapolation of the log μ vs T relationship to any predetermined viscosity in the range of 10^{13}–10^{18} Pa s is based on circular reasoning. Mathematically, and like the Arrhenius equation, the WLF model has the built-in assumption that the temperature effect is *qualitatively* the same at every temperature range and hence that it can be used for extrapolation to both low and high temperatures. Unlike the Arrhenius equation's 'energy of activation', the WLF model's coefficients C_1 and C_2 do not have an obvious or direct kinetic interpretation since they depend, inherently, on the chosen reference temperature. Nevertheless, once determined for one reference temperature, they can be recalculated for any other reference temperature by the transformations

$$C_{1b} = C_{1a}C_{2a}/(C_{2a} + \delta) \tag{8}$$

and

$$C_{2b} = C_{2a} + \delta \tag{9}$$

where C_{1a} and C_{2a} are the constants determined at a temperature T_a, and C_{1b} and C_{2b} are the transformed constants at a temperature $T_b = T_a + \delta$. (The temperature shift δ can be either positive or negative.) Thus, by selecting a common reference temperature and recalculating the model's coefficients, the rate *versus* T relationships of different materials or systems can be quantitatively compared.

AN ALTERNATIVE APPROACH

It is not inconceivable that at certain temperature levels the system in question is practically inert and only at a high enough temperature does its activity accelerate. A case in point is microbial inactivation. It is not unreasonable to expect that up to a certain characteristic temperature, which is affected by the medium composition, pH and other factors, microorganisms and particularly spores are not destroyed (and may even grow). The same can be said of the progress of oxidation and browning reactions. They can be practically undetected at low temperatures but very noticeable at processing temperatures such as in drying. ('Practically' is intentionally used here to emphasise that all the statements pertain only to temperature levels and time scales that have practical consequences.) In such cases the temperature effect can be expressed in the form of a log-logistic relationship[17,18]

$$Y = \ln(1 + \exp[c(T - T_c)]) \tag{10}$$

where Y is the rate parameter in question and c and T_c are constants. (As in similar equations, to make the model dimensionally consistent, Y is divided by a unit rate, which renders its numerical values the same as the measured ones.) The reader will notice (Fig 1) that, according to this model, as long as $T \ll T_c$, $Y \sim 0$, while at $T \gg T_c$, $Y = c(T - T_c)$, ie it increases linearly.

The increase, however, need not be linear in all systems and therefore a more general version of the model can be written in the form

$$Y = \ln\{1 + \exp[c(T - T_c)]\}^m \tag{11}$$

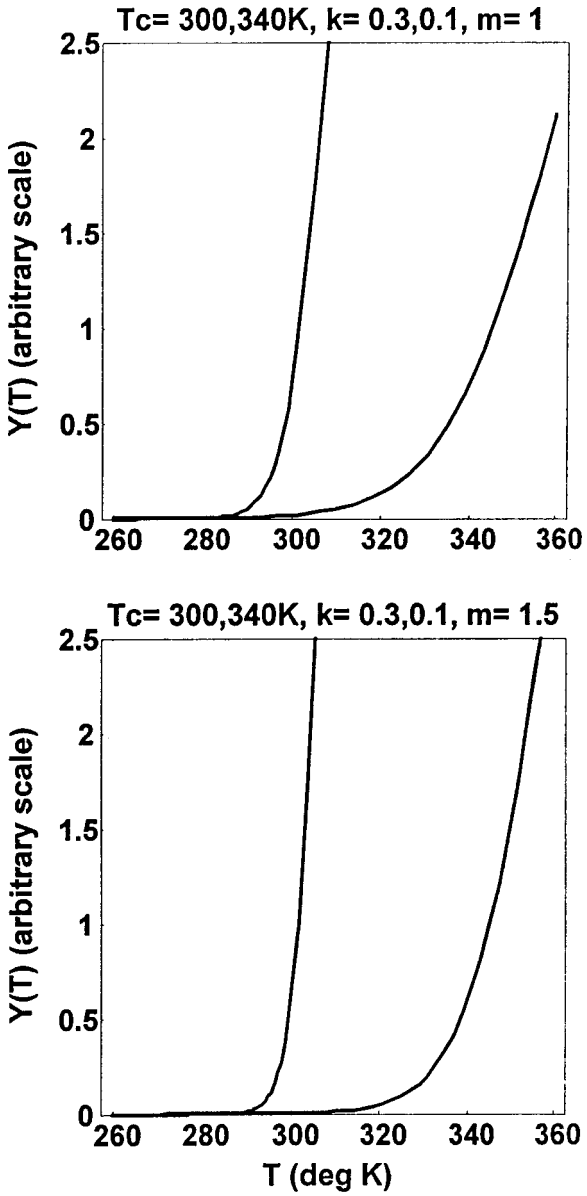

Figure 1. Generated rate *versus* temperature relationships using eqn (10), $m=1$ (top) and $m>1$ (bottom), and eqn (11) as models.

where m is a power expected to be, but need not always be, higher than one. As before, as long as $T \ll T_c$, $Y \sim 0$. However, at $T \gg T_c$ the Y *versus* T relationship would have an upward concavity if $m>1$. A model in the form of eqn (10) or (11) is purely empirical or phenomenological; that is, it is not based on any analogy to a simple chemical reaction as in the Arrhenius model or to the viscosity of polymer melts as in the WLF model. It is especially formulated to identify the temperature level at which changes in the food system start their acceleration. Also, since the rate–temperature relationship is expressed as $Y=Y(T)$ and not $\ln Y(T)$ or $\log_{10} Y(T)$ *versus* T as in the Arrhenius and WLF models respectively, the excessive weight usually given to the low-temperature range is thus avoided. The questions that arise are whether eqn (10) or (11) can describe rate–temperature relationships of real food systems as effectively as the Arrhenius and WLF models and whether all three are mutually exclusive models except for some rare special cases. The following will address these issues.

THE ALTERNATIVE MODEL'S APPLICABILITY

The fit of the model to three kinds of published rate constant *versus* temperature relationships is demonstrated in Figs 2–7. The fit parameters are listed in Table 1. Except in two cases, all the calculations were made and the plots produced using Mathematica 4[R] (Wolfram Research, Champaign, IL, USA). In two cases the fit was done using Systat 5.01 (Systat Inc,

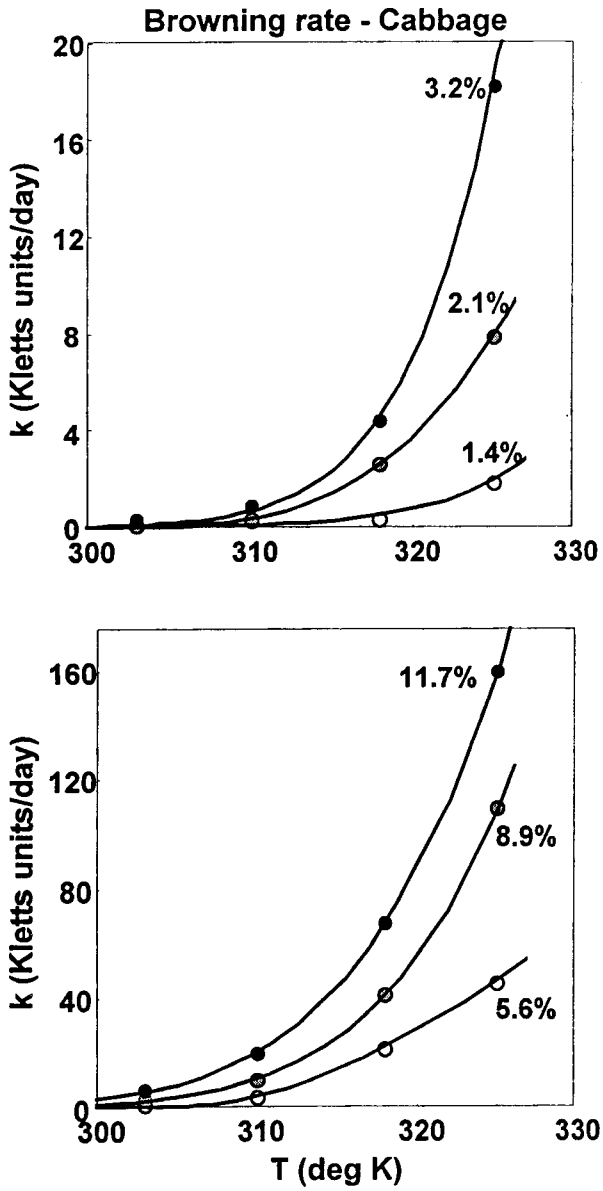

Figure 2. Published browning rate–temperature relationships of dried cabbage with different moisture contents fitted with eqn (11) as a model. The experimental data are from Mizrahi *et al.*[20] The regression parameters are given in Table 1.

System	T_c (K)	c (K^{-1})	m	χ^2	Data source
Browning					
Cabbage 1.4% M	294	0.020	15.3	0.041	Mizrahi *et al*[20]
Cabbage 2.1% M	311	0.198	1.98	0.003	
Cabbage 3.2% M	305	0.082	4.89	0.096	
Cabbage 5.6% M	306	0.511	1.67	1.098	
Cabbage 8.9% M	294	0.095	4.23	0.394	
Cabbage 11.7% M	289	0.092	4.22	0.525	
Potato 15% M	323	0.0173	9.70	7.8×10^{-5}	Hendel *et al*[21]
Potato 9.4% M	312	0.0119	14.8	9.5×10^{-5}	
Potato 4.9% M	313	0.0120	19.3	6.9×10^{-7}	
Potato + sulphite 9.2% M	301	0.017	14.5	3.5×10^{-5}	Legault *et al*[22]
Potato + sulphite 7.6% M	311	0.026	11.8	3.0×10^{-6}	
Potato + sulphite 5.3% M	305	0.017	16.5	1.1×10^{-5}	
Model systems					
Lact:Amio:Lys a_w = 0.12	385	0.4900	1.0[a]	0.154	Karmas *et al*[5]
	377	0.0980	2.30	0.029	
Lact:Amio:Lys a_w = 0.23	383	0.4530	1.0[a]	0.292	
	370	0.0480	4.10	0.162	
Lact:Amio:Lys a_w = 0.33	381	0.3070	1.0[a]	0.058	
	372	0.0570	3.30	0.005	
PVP:Glu:Gly (20:0.5:0.5)	319	0.0117	13.8	2.8×10^{-5}	
Microbial inactivation					
Salmonella	67[b]	0.2944	1.20	0.021	Mattick *et al*[23]
Listeria	61[b]	1.3405	1.0[a]	0.190	Stephens *et al*[24]
C botulinum (spores)	102[b]	0.3000	1.0[a]	0.243	Anderson *et al*[25]
Flowability					
Melted cheese	34[b]	0.6021	1.0[a]	0.215	Campanella *et al*[26]
Melted fructose	65[b]	0.2091	2.70	0.543	Parker and Ollett[4]

Table 1. Regression parameters of published rate *versus* temperature relationships fitted with eqn (10) or (11) as a model

[a] Eqn (10).
[b] °C.

Evanston, IL, USA), which had a more suitable algorithm for the particular data sets. (Either way, because of the limited number of data points and occasional scatter, a close initial estimate of parameters was needed.) According to the original authors, the browning rates in both the dried foods and model systems had been determined by optical measurements. The flowability of the fructose and melted cheese was calculated as the reciprocal of the shear and elongational viscosity respectively. In contrast with viscosity, which with very few exceptions sharply declines as temperature increases, flowability rises with temperature. The microbial inactivation data were obtained by fitting published survival curves at different temperatures to the model[19]

$$\log_{10} S(t) = -b(T)t^{n(T)} \qquad (12)$$

where $S(t) = N(t)/N_0$ is the survival ratio and $b(T)$ and $n(T)$ are temperature-dependent coefficients. Although $n(T)$ especially of the *Clostridium* and *Salmonella* was far from being constant, the model (eqn (10) or (11)) was only applied to $b(T)$. The reason is that when $b(T) \sim 0$, hardly any inactivation takes place on a practical time scale regardless of the magnitude of $n(T)$. Since the main purpose of the discussed model (eqn (10) or (11)) is to identify the temperature range where the activity accelerates, ignoring the changes in $n(T)$ was justified. Obviously, if one wants to quantify the exact progress of the inactivation process itself, $n(T)$ must be taken into account too.

Figs 2–7 and Table 1 demonstrate that the model's fit was highly satisfactory for *all* the systems examined. Moreover, in several cases the two-parameter version of the model, ie eqn (10), was quite adequate. The applicability of the general form of the model (eqn (11)) to such a diverse group of systems suggests that rate phenomena can indeed have two kinetic regimes with a smooth transition between them. The model seems to be a useful mathematical tool to identify this transition region and quantify the rate of acceleration at the high-temperature regime. The model is clearly *inadequate* to account for changes that occur at (relatively) low temperatures owing to lack of sensitivity. How the transition region which is identified by this model relates to physicochemical events or mechanisms at the molecular or cellular level remains to be seen. The model in the form of eqn (10) or (11) is only a mathematical tool which describes the expression of

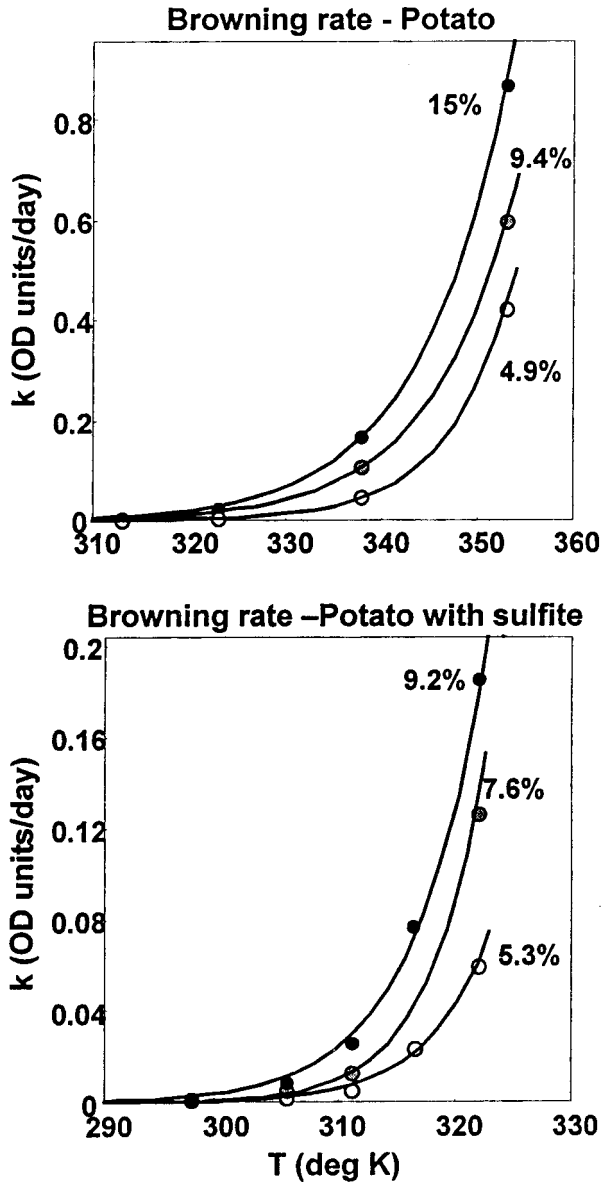

Figure 3. Published browning rate–temperature relationships of dried potato with and without added sulphite at different moisture contents fitted with eqn (11) as a model. The experimental data are from Hendel *et al*[21] (top) and Legault *et al*[22] (bottom). The regression parameters are given in Table 1.

such events or mechanisms at the macroscopic level. These events or mechanisms are most probably specific rather than general, despite the qualitative similarities in their overall manifestation. The reader should be reminded that the model is purely empirical and based solely on the system's observed response. It does not require the assumption that there is such a thing as a temperature-independent 'energy of activation' or a unique reference temperature like T_g. The model's parameters T_c, c and m may well be associated with the energy of activation of local reactions or with glass and other temperature-induced phase transitions. However, such an association can only be established by *independent chemical and/or physical assays* and not from the shape of the rate–temperature curve. As in many other systems, the shape of the curve alone does not contain enough information to confirm a proposed mechanism, although sometimes it can exclude certain alternatives (see below).

COMPARISON OF THE MODEL WITH THE ARRHENIUS AND WLF EQUATIONS

Can either the Arrhenius or WLF equation and the described model fit the same experimental data? The relationships shown in Figs 2–7 are mostly from publications where it has been claimed that they obey either the Arrhenius equation or WLF model. That these two are incompatible, at least at a certain temperature range, is well known. For example, a non-linear $\ln Y(T)$ *versus* $1/T$ relationship which is sufficient to invalidate the Arrhenius equation can frequently be fitted with the WLF equation if it has an upward concavity.

The compatibility of the alternative model (eqn (10) or (11)) with the Arrhenius and WLF equations was tested by generating Y *versus* T data with one and fitting them with the other. To demonstrate the comparison under emulated realistic conditions, the data were generated with random noise of controlled amplitude. The noise was produced with random numbers that had a normal (Gaussian) distribution. Thus the probability of a deviation from the 'theoretical' or 'presumably correct' value diminished exponentially with the deviation's magnitude. Mathematically, the generated values were produced by

$$Y_{\text{generated}} = Y_{\text{theoretical}}(1 + sZ_{\text{nT}}) \qquad (13)$$

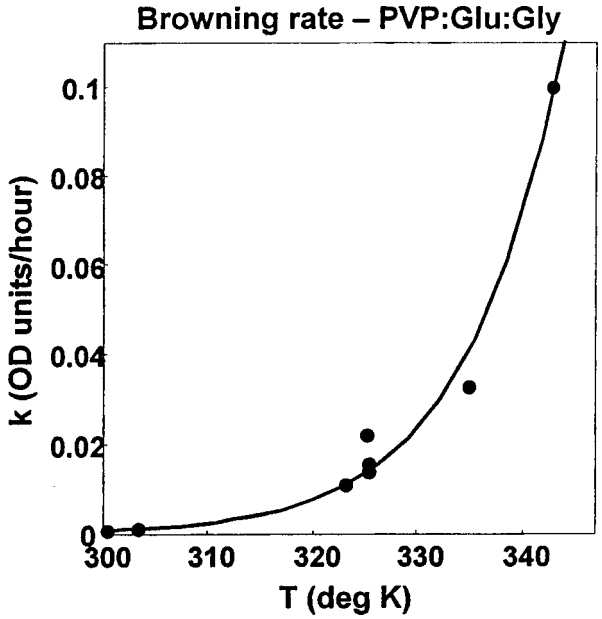

Figure 4. Published browning rate–temperature relationships of a PVP:glucose:glycine model system fitted with eqn (11) as a model. The experimental data are from Karmas *et al.*[5] The regression parameters are given in Table 1.

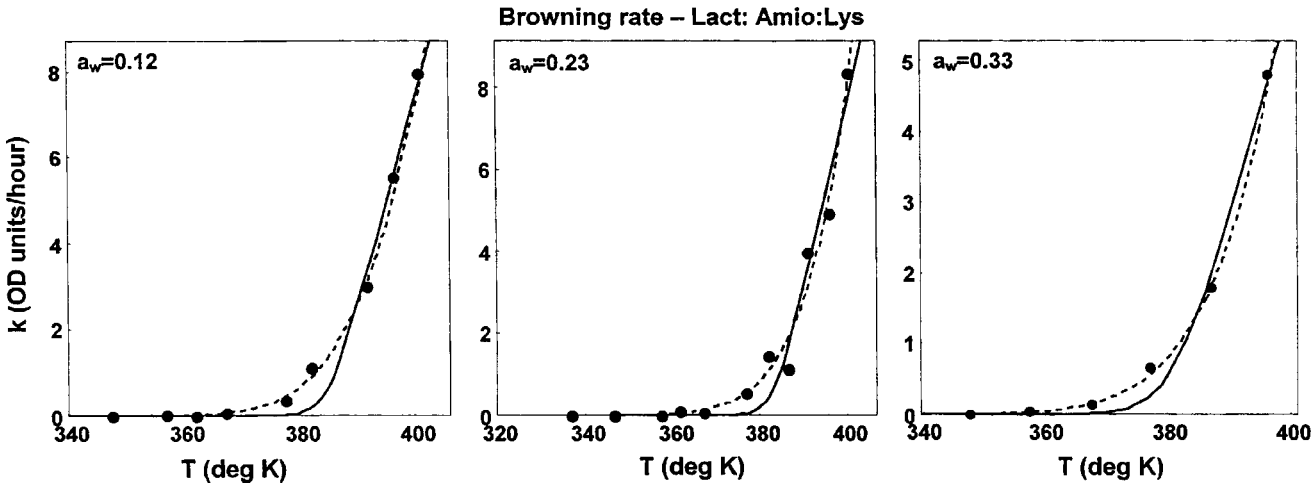

Figure 5. Published browning rate–temperature relationships of a lactose:amylose:lysine model system with different levels of water activity fitted with eqns (10) (full lines) and (11) (broken lines) as models. The experimental data are from Karmas *et al.*[5] The regression parameters are given in Table 1.

where s is a constant (the standard deviation of the noise around the theoretical value) and Z_{nT} is a random number with a standard normal distribution ($\mu = 0$, $\sigma = 1$). Examples of the fit of the model to data produced with the Arrhenius and WLF equations as models are given in Figs 8–11. They demonstrate that eqns (10) and (11) and the Arrhenius or WLF equation need not be mutually exclusive models and that they can describe the same set of data with a similar fit. The difference between the models, as already mentioned, is the relative weight given to the data at the low- and high-temperature regions. The figures also demonstrate that while data created with the two traditional models can almost always be fitted with the new model (Figs 8 and 9), the opposite need not be generally true (Fig 10). When the model is used with $m \neq 1$ (eqn (11), this would not be surprising, of course, because it is usually difficult to fit data generated with a three-parameter model with a two-parameter expression.

CONCLUDING REMARKS

The Arrhenius and WLF equations do not provide a unique description of rate–temperature relations in food systems, and alternative models can have a similar or even better fit to experimental data. The formulation of these two traditional models as logarithmic relationships makes them particularly sensitive to rates at the lower end of the examined temperature range. In many systems this region is of special interest (eg flowability at low temperatures or

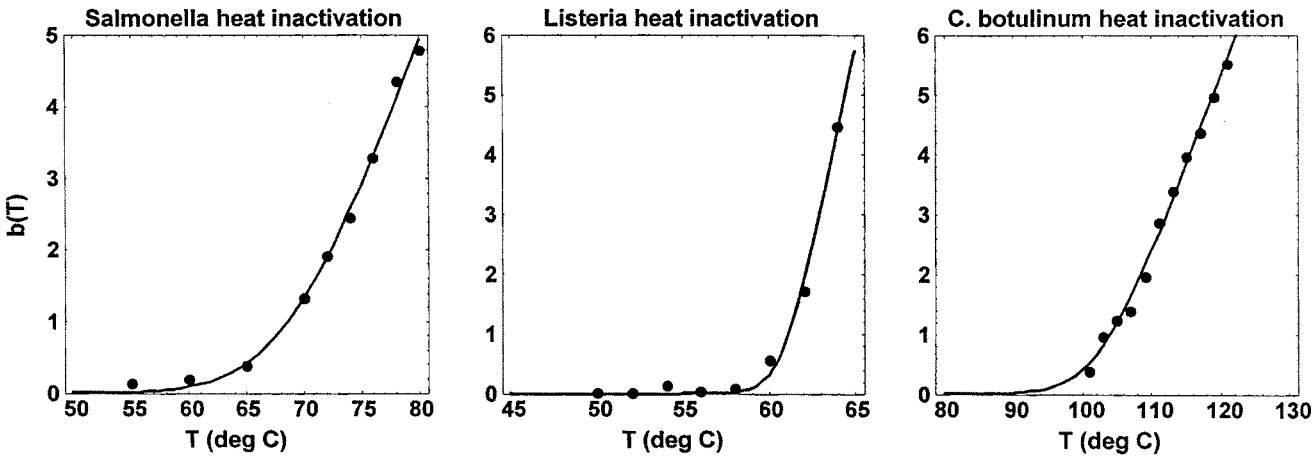

Figure 6. Published inactivation parameter $b(T)$ *versus* temperature relationships of *Salmonella*. *Listeria* and *Clostridium botulinum* fitted with eqn (10) as a model. Data are from Mattick *et al*,[23] Stephens *et al*[24] and Anderson *et al*[25] respectively. The regression coefficients are listed in Table 1.

biochemical reactions in stored foods), in which case these two models would be most useful. However, there are processes, such as microbial or enzymatic inactivation, where the effects of exposure are inconsequential at low temperatures. For these, identification of the temperature range where the acceleration commences can be of paramount importance from a practical point of view. The log-logistic model described in this work is formulated in such a way that one of its parameters, T_c, is a marker of this temperature range. Its other parameters, c and m, account for the steepness of the rate–temperature relationship beyond T_c. Unlike in the Arrhenius and WLF models, the activity increase is expressed in terms of rate *versus* temperature and not log(rate) *versus* temperature. Thus, when experimental data are

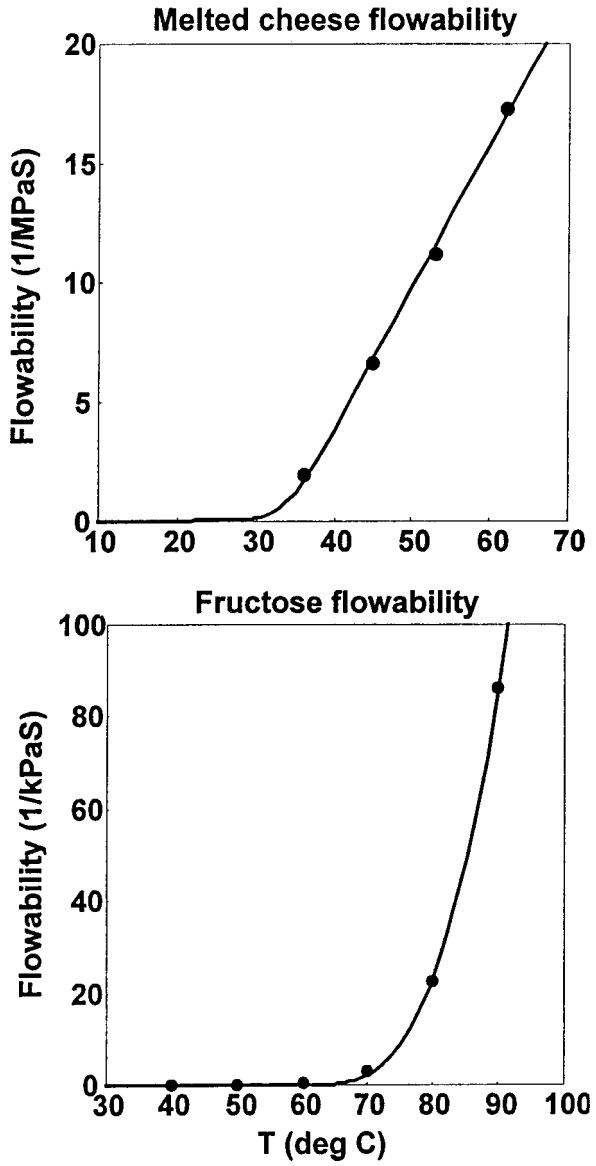

Figure 7. Published flowability *versus* temperature relationships of melted cheese and fructose fitted with eqns (10) (top) and (11) (bottom) as models. The experimental data are from Campanella *et al*[26] and Parker and Ollett[4] respectively. The regression coefficients are listed in Table 1.

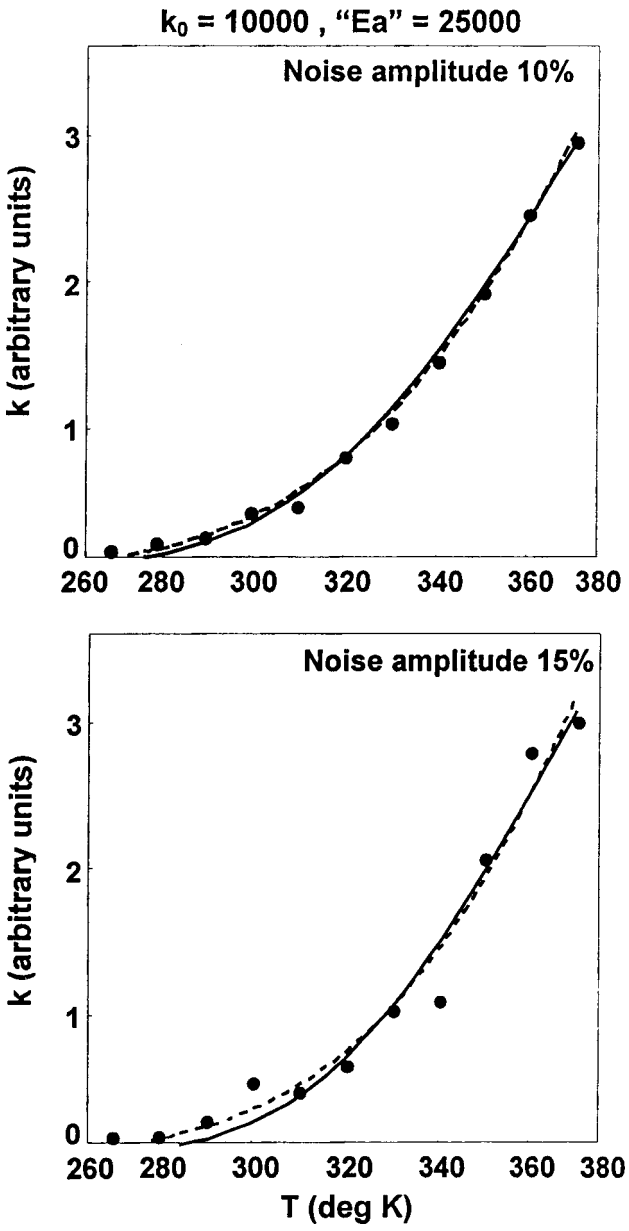

Figure 8. Simulated rate *versus* temperature relationships generated with the Arrhenius equation fitted with eqns (10) (full lines) and (11) (broken lines) as models.

fitted with this model, the magnitude of its constants T_c, c and m and the quality of the interpolations calculated with it are expected to be much less affected by errors or deviations at the low end of the temperature range. Unlike the Arrhenius equation, this model is not built on the assumption that a large class of unrelated rate phenomena share a kinetics that is analogous to that of simple chemical reactions. Thus the 'energy of activation', which has rarely, if ever, been determined independently, is not included in the model. The energetics of different systems can still be compared, though, albeit in terms of their respective T_c's, ie the temperature range where they are activated. Similarly, and unlike the WLF equation, the model has no reference temperature like the glass transition

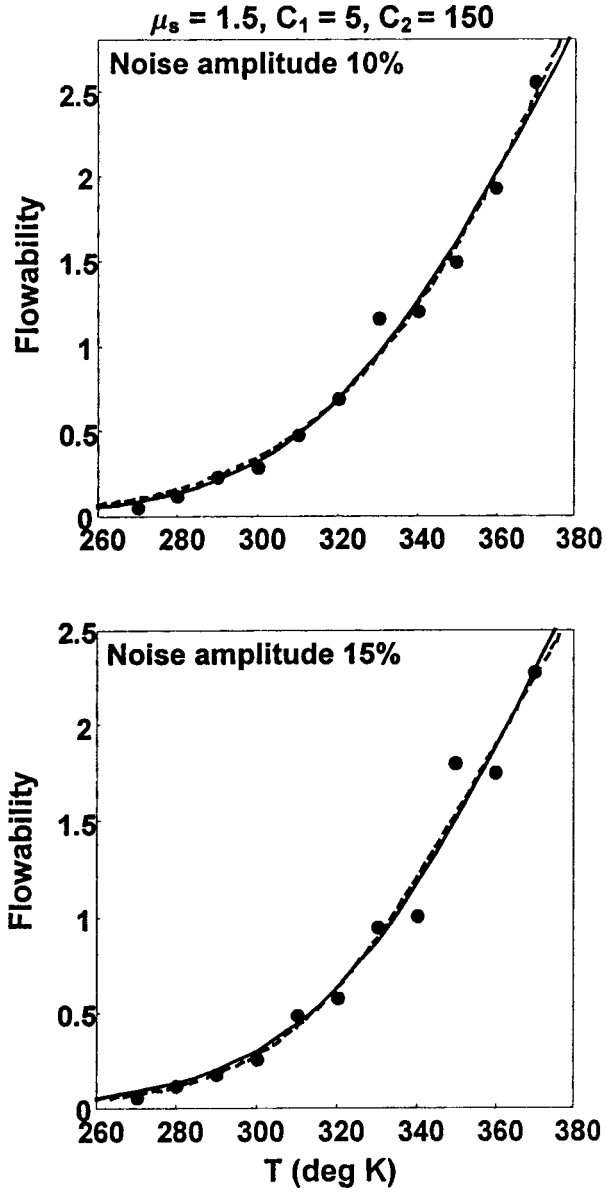

Figure 9. Simulated flowability *versus* temperature relationships generated with the WLF equation fitted with eqns (10) (full lines) and (11) (broken lines) as models.

temperature T_g, whose very physical existence is a matter of a debate. The model's format and the magnitude of its constants are all determined by the actual behaviour of the system in question and not from analogies to other systems, which may or may not exist. But again, the described model, like the Arrhenius and WLF equations, is also not unique. Thus, if there are applications for which eqn (11) is inadequate, it can and should be replaced by a model which does capture the pertinent aspects of the rate–temperature relationship correctly. Obviously, the mathematical structure and parameters of any such alternative model would be a manifestation of mechanisms operating at the molecular or cellular level. Nevertheless, the relationship between these and the underlying mechanisms would have to be established and confirmed by *independent tests*. Also, because of the nature of non-linear regression, the fitted model's parameters may depend on the number of available data points and their scatter. Consequently, a correct identification of T_c, and a reliable characterisation of the rate–temperature relationship beyond it, can only be made if the experimental data cover a sufficiently large temperature range below and above the transition temperature region.

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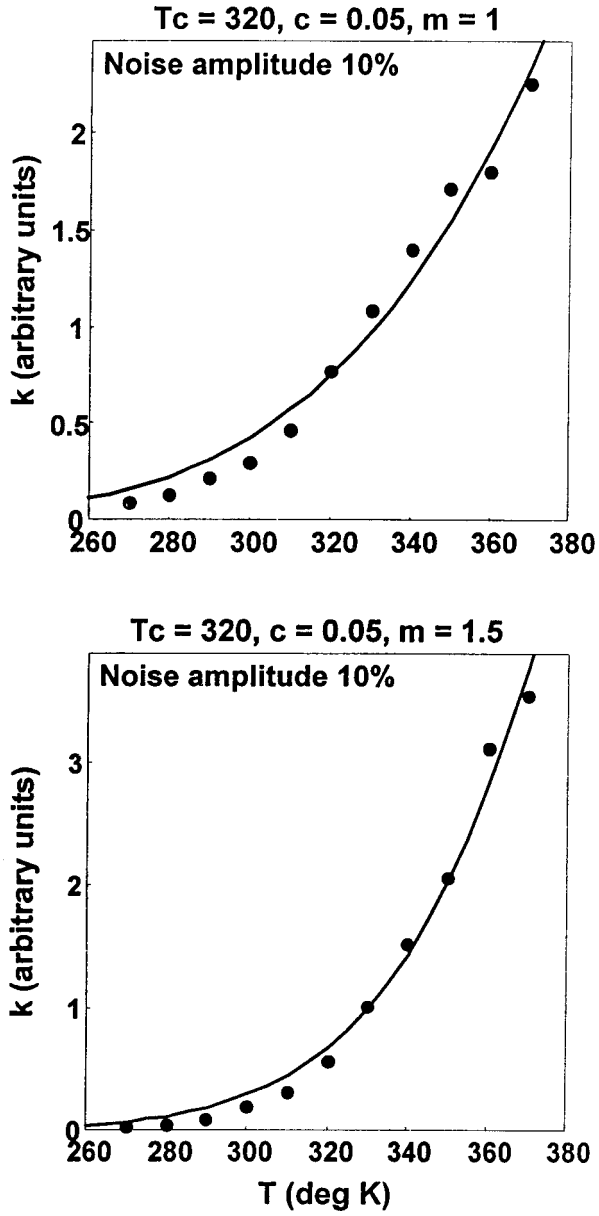

Figure 10. Simulated rate *versus* temperature relationships generated with eqns (10) (top) and (11) (bottom) fitted with the Arrhenius equation as a model.

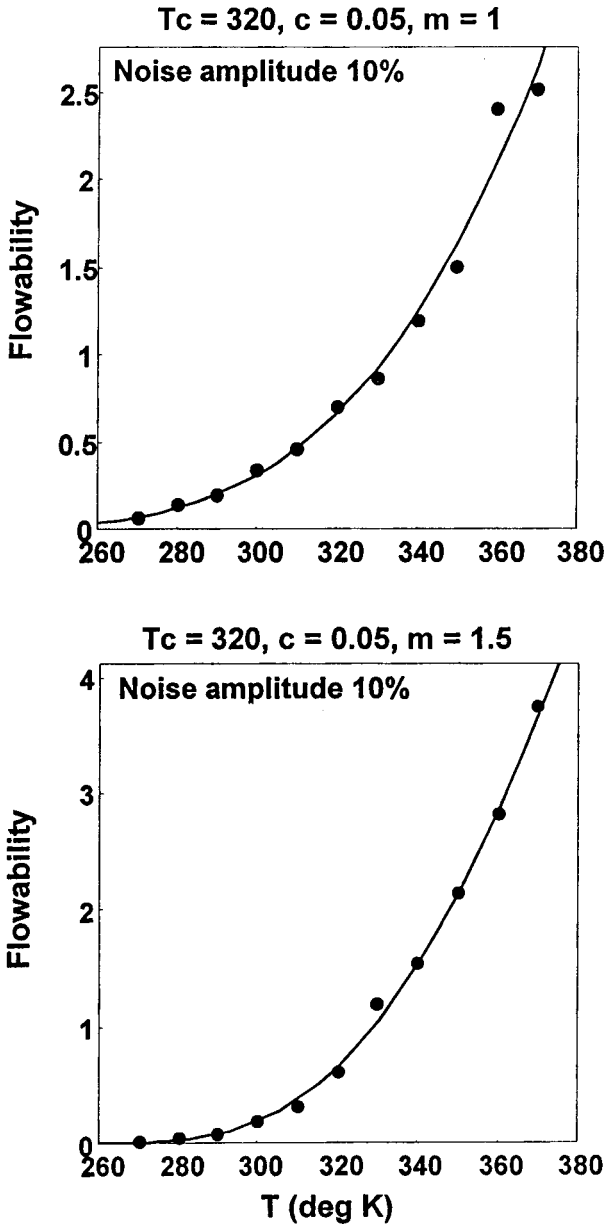

Figure 11. Simulated flowability *versus* temperature relationships generated with eqns (10) (top) and (11) (bottom) fitted with the WLF equation as a model.

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