Temperature–viscosity models reassessed

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ABSTRACT

The temperature effect on viscosity of liquid and semi-liquid foods has been traditionally described by the Arrhenius equation, a few other mathematical models, and more recently by the WLF and VTF (or VFT) equations. The essence of the Arrhenius equation is that the viscosity is proportional to the absolute temperature's reciprocal and governed by a single parameter, namely, the energy of activation. However, if the absolute temperature in K in the Arrhenius equation is replaced by $T + b$ where both T and the adjustable b are in °C, the result is a two-parameter model, which has superior fit to experimental viscosity–temperature data. This modified version of the Arrhenius equation is also mathematically equal to the WLF and VTF equations, which are known to be equal to each other. Thus, despite their dissimilar appearances all three equations are essentially the same model, and when used to fit experimental temperature–viscosity data render exactly the same very high regression coefficient. It is shown that three new hybrid two-parameter mathematical models, whose formulation bears little resemblance to any of the conventional models, can also have excellent fit with $r^2 \sim 1$. This is demonstrated by comparing the various models' regression coefficients to published viscosity–temperature relationships of 40% sucrose solution, soybean oil, and 70°Bx pear juice concentrate at different temperature ranges. Also compared are reconstructed temperature–viscosity curves using parameters calculated directly from 2 or 3 data points and fitted curves obtained by nonlinear regression using a larger number of experimental viscosity measurements.

Introduction

The temperature–viscosity relationship of fluids plays an important role in many fields of technology. Therefore, and not surprisingly, there are quite a few mathematical models to describe the effect of temperature on the viscosity of fluids, from gases, such as air, to pure liquids and lubricants, and from polymer melts to molten metals and rocks. In liquid and semi-liquid foods, the viscosity or consistency is not only a major sensory textural property but also plays an important role in their processing and preservation.

Traditionally, the effect of temperature on a liquid food's Newtonian viscosity or its apparent viscosity at a specified shear rate has been described by the Arrhenius equation. This temperature–viscosity model has a single adjustable parameter, namely, the "energy of activation," and it can be written in the form:

$$\text{Ln}\left[\frac{\mu(T)}{\mu_{T_{\text{ref}}}}\right] = \frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right), \qquad (1)$$

where $\mu(T)$ is the Newtonian or apparent viscosity at an absolute temperature T (in K) and $\mu_{T_{\text{ref}}}$ at an arbitrary absolute reference temperature T_{ref}. E_a on the right side of the equation is the energy of activation, usually expressed in kJ or kcal per mole, and R is the Universal gas constant in corresponding units (e.g., Telis et al., 2007; Rao, 2014). One of the implications of Equation (1) is

a linear $\text{Ln}[\mu(T)]$ vs. $1/T$ plot (e.g., Yanniotis et al., 2006), from whose slope E_a has been traditionally estimated, usually without independent verification, see below.

Evidence of systems where the $\text{Ln}[\mu(T)]$ vs. $1/T$ plot is curvilinear has resulted in the development of alternative non-Arrhenius viscosity–temperature models. The most familiar of these is the empirical Williams—Landel–Ferry (WLF) model adopted from Polymer Science, which for our purpose can be written in the form (e.g., Maltini and Anese, 1995; Sopade et al., 2002; Recondo et al., 2006; Rao, 2014):

$$\text{Log}_{10}\left[\frac{\mu(T)}{\mu_{T_{\text{ref}}}}\right] = -\frac{C_1(T - T_{\text{ref}})}{C_2 + (T - T_{\text{ref}})}, \qquad (2)$$

where C_1 and C_2 are the two adjustable parameters. Following the Polymer Science literature, the "glass transition temperature," T_g, has been frequently chosen as the reference temperature (e.g., Ollett and Parker, 1990; Kerr and Reid, 1994; Recondo et al., 2006). Since issues concerning the meaning of T_g in food rheology are outside the scope of this review, only its role as a parameter in temperature–viscosity models will be addressed. Notice that regardless of how the chosen T_{ref} in the WLF model it is defined, it must always to be sufficiently low in order to avoid a sign change in the viscosities ratio's logarithm.

Otherwise, the model will render absurd predictions of a liquid's rheological behavior at low temperatures.

A recent and less familiar alternative model to the Arrhenius equation has been the three-parameter Vogel–Tamman–Fulcher (VTF) equation, also known as the Vogel-Fulcher-Tamman (VFT) equation (e.g., Kerr and Reid, 1994; Rampp et al., 2000; Sopade et al., 2002; Recondo et al., 2006; Monkos, 2008; Rao, 2014), which can be written in the form:

$$\mathrm{Ln}[\mu(T)] = A_{\mathrm{VTF}} + \frac{B_{\mathrm{VTF}}}{T - T_0}, \tag{3}$$

where the three adjustable parameters are A_{VTF}, B_{VTF}, and T_0. Although known to be equal to the WLF equation (Angel, 1997), the VTF equation has been frequently treated as an independent model in the literature on the viscosity of food and non-food materials, see below.

Other viscosity–temperature models include the exponential model (Saravacos, 1977), which can be written in the form

$$\mathrm{Log}[\mu(T)] = A - \mathrm{B}T, \tag{4}$$

where T is °C in A and B are constants, the power law equation (Ollett and Parker, 1990; Recondo et al., 2006; Fasina et al., 2008), which can be written in the form:

$$\mu(T) = k(T - T_{\mathrm{ref}})^{-m}, \tag{5}$$

where $T > T_{ref}$, and k and m are constants, and versions of the Arrhenius equation with various added terms. For other historic mathematical models of temperature–viscosity relationships, see Higgins (2014).

The original Arrhenius equation (Equation (1)) is still the most commonly referred to mathematical model of the temperature–viscosity relationships of foods and non-food materials primarily of pure compounds and solutions. The Arrhenius equation's attractiveness over the other temperature–viscosity models, such as Equations (2)–(5), stems from its original derivation from statistical mechanical considerations, and from that the fluid's flowability is expressed in term of activation energy, which links it to the fundamentals of physical chemistry and to mechanisms that operate at the molecular level (e.g., Mizrahi and Berk, 1972). Also, the Arrhenius model has a single adjustable parameter; the said energy of activation E_a, while the other models have two or three adjustable parameters whose physical interpretation is less straightforward. When it comes to fitting experimental temperature–viscosity data and the accuracy of a model's predictions, its mathematical formulation and number of adjustable parameters play a crucial role, which is the focus of this review. To start, let us examine the performance of the Arrhenius and its two main alternatives from a purely formalistic viewpoint.

The original and modified Arrhenius equations

Apart from the obvious inconvenience of converting the temperatures in °C to absolute temperature reciprocals (K^{-1}), and thereby compressing and reversing the temperature scale, the application of the Arrhenius model to viscosity estimation at different temperatures raises several fundamental issues too. Since the energy of activation, E_a, is expressed in energy per mole units, the most prominent among these issues is the physical meaning of a "mole" in the context of complex liquid foods such as fruit juices and their concentrates, semi-gelled dairy product such as stirred yogurt, or ketchup and other tomato products. This issue can be circumvented if Equation (1) is treated as an empirical model and the term E_a/R is replaced by a temperature-sensitivity parameter a having temperature dimension and °C units. A not a lesser issue is whether the temperature scale conversion to absolute temperature expressed in K is meaningful and really necessary. Is 0 K, or −273.16°C, a relevant point of reference to liquid foods' flowability at the temperatures of their consumption, storage, and/or processing? If not really, then at least from a formalistic viewpoint, the added 273.16°C to the temperature in °C can be considered what statisticians call a "nuisance factor," i.e., a constant whose magnitude (within a reasonable range) has little or no effect on the model's fit and performance. The rationale behind this suggestion is the observation that if we replace the term T+273.16°C in the original Arrhenius equation by T+b, where b (in °C) assumes any arbitrary value, in the range 200 to 400°C, say, the Arrhenius model will exhibit the same behavior, including rendering an almost perfectly linear $\mathrm{Ln}[\mu(T)]$ vs. $1/(T+b)$ plot (Peleg et al., 2012). This property of the Arrhenius equation can be visualized with a freely downloadable interactive Wolfram Demonstration where one can generate fit data with various values of b, open http://demonstrations.wolfram.com/ArrheniusVersusExponentialModelForChemicalReactions/. [To download the (also free) Wolfram CDF Player that runs the Demonstration, and over 11,200 other Demonstrations to date, follow the instructions on the screen.]

One can also argue that a liquid food's flowability at room temperature or when heated has more to do with the melting point than with the Universal 0 K, as in the case of the glass transition temperature of polymers. Again, as in the physical interpretation of a T_g, the meaning of a characteristic melting point, T_m, in the context of oils and fats, for examples, which freeze and melt over a considerable temperature range, or of sugar-rich fruit juice concentrates, where ice separates during freezing, should not concern us here. Could b be treated as a physical parameter? An answer to this question will require a special study and it is outside the scope of this review. But even if the absolute temperature replacement by an adjustable parameter b is treated merely as a mathematical device to retain the Arrhenius equation's structure while improving its fit and predictions, the properties of the resulting modified model seem to be worth further evaluation. Notice that according to the original Arrhenius equation, only at $T \to 0$ K, $\mu(T) \to \infty$, i.e., complete solidification, while at $T \to \infty$, $\mathrm{Ln}[\mu(T)/\mu(T_{\mathrm{ref}})] \to -E_a/(RT_{\mathrm{ref}})$, i.e., $\mu(\infty) \to$ constant > 0 and not zero. However, these two issues have no practical consequences. At the low end of the temperature range, one can argue that viscosity on the order of 10^{15} Pa s, say, can be treated as solidity for all practical purposes, at least for food applications. At the high end of the range, any impact of the viscosity's diminishing temperature sensitivity, which the Arrhenius models implies, would be felt only at temperatures that are well above any encountered in food processing, consumption, transportation, or storage.

The modified or revised Arrhenius equation can be written in the form (Peleg et al., 2012):

$$\text{Ln}\left[\frac{\mu(T)}{\mu_{T_{\text{ref}}}}\right] = a\left(\frac{1}{T+b} - \frac{1}{T_{\text{ref}}+b}\right), \tag{6}$$

where T is in $°C$ and a and b are the adjustable parameters having $°C$ units too. Similarly to the original version of the equation, when $T \rightarrow$, $\text{Ln}[\mu(T)/\mu(T_{\text{ref}})] \rightarrow -a/(T_{\text{ref}} + b)$, i.e., $\mu(\infty) \rightarrow$ constant > 0, which again has no practical consequences. However, in contrast with the Arrhenius equation's original version, when $b < 273.16°C$ and $T \rightarrow -b$ (in $°C$), $\mu(-b) \rightarrow \infty$, i.e., the modified model implies complete solidification at temperatures higher than the absolute zero, at least qualitatively. Here again, though, since extremely high viscosity can be considered equivalent to solidity, this issue need not have any practical implications at least when it comes to foods.

The exponential model

According to Wikipedia, it was the famous Reynolds who was the first to propose the exponential model, which he presented in the form:

$$\mu(T) = \mu_0\text{Exp}(-cT), \tag{7}$$

where μ_0 and c are its adjustable coefficients. Equation (7) is equal to Equation (4) used by Saravacos (1977) for a variety of fruit juices and purees, where $\mu_0 = \text{Exp}(A)$ and $c = B$.

The exponential model can also be written in a form that includes T_{ref} and $\mu_{T_{\text{ref}}}$, i.e.,

$$\text{Ln}\left[\frac{\mu(T)}{\mu_{T_{\text{ref}}}}\right] = c(T_{\text{ref}} - T), \tag{8}$$

where $\mu_0 = \mu_{T_{\text{ref}}}\text{Exp}(cT_{\text{ref}})$. The attraction of Equation (8) is that its right side is the first term of the Taylor series expansion of $\text{Ln}[\mu(T)/\mu(T_{\text{ref}})]$ at T_{ref} when defined by the original or revised versions of the Arrhenius equation, i.e., by Equation (1) or Equation (6). Since the series converges rapidly, the exponential and modified Arrhenius models could be used interchangeably in degradation kinetics (Peleg et al., 2017). As far as fitting experimental temperature–viscosity data is concerned, however, the original Arrhenius model (Equation (1)) has an inherent advantage over the exponential model (Equation (8)) because of the added "nuisance factor," $273.16°C$, and more so when b becomes an adjustable parameter (Equation (6)), which makes the Arrhenius equation a two-parameter model. To compensate for this inherent disadvantage, see below, one can add a small quadratic correction factor to the exponential model, which then becomes

$$\text{Ln}\left[\frac{\mu(T)}{\mu_{T_{\text{ref}}}}\right] = -c_1(T - T_{\text{ref}}) + c_2(T - T_{\text{ref}})^2, \tag{9}$$

where c_1 and c_2 are the two adjustable parameters. This model can have an almost perfect fit, see below, comparable to that of the revised Arrhenius and the other two-parameter models.

However, its very serious drawback is that because of the added term it predicts absurd viscosity rise at $T > T_{\text{ref}} + c_1/2c_2$. Therefore, it can only be safely used for interpolation but not for extrapolation to high temperatures.

The WLF, VTF (VFT), and modified Arrhenius models

Since the original WLF model (Equation (2)) already has two adjustable parameters, C_1 and C_2, and the VTF or VFT model (Equation (3)) has three, namely A_{VTF}, B_{VTF}, and T_0, they need no modification for comparing their fits and predictions' accuracy to those of the other models. As already mentioned, the WLF and VTF are known to be equal despite their dissimilar appearance and different number of adjustable parameters (Angel 1997). A formal proof of these two models identity is given in the Appendix. Less obvious is that either and both models are also equal to the modified Arrhenius model (Equation (6)). A proof of these identities is also given in the Appendix. These identities imply that when any experimental temperature–viscosity dataset is fitted by the three models, the regression coefficient is expected to be exactly the same and that the regression parameters of any of the three models can be used to calculate those of the other two using the formulas provided in the Appendix, see below.

Notice that all three models, or versions of the modified Arrhenius equations (Equation (6)), entail that there is a temperature, $T_{\text{min}} > -273.16°C$ at which, $\mu(T_{\text{min}}) \rightarrow \infty$. Hence, they all become meaningless below this T_{min}, a consideration that should be taken into account when choosing the reference temperature for fitting experimental data, and attempting to predict viscosities at low temperatures by extrapolation, see below.

Hybrid temperature–viscosity models

In principle, one can construct ad hoc empirical models that combine the properties of the above-mentioned models. Two examples are an exponential-power-law (EP) model, which can be written in the form:

$$\text{Ln}\left[\frac{\mu(T)}{\mu_{T_{\text{min}}}}\right] = -c_{\text{EP}}(T - T_{\text{min}})^{m_{\text{EP}}} \tag{10}$$

and a reciprocal-power-law (RP) model, which can be written in the form:

$$\frac{\mu(T)}{\mu_{T_{\text{min}}}} = \frac{1}{1 + c_{\text{RP}}(T - T_{\text{min}})^{m_{\text{RP}}}}, \tag{11}$$

where T_{min} is an arbitrary low temperature, lower than the lowest one in the fitted dataset, and the c's and m's are the adjustable parameters. Notice that both models imply that when $T \rightarrow \infty$, $\mu(T) \rightarrow 0$. However, they also become physically meaningless, i.e., producing a complex viscosity ratio, when $T < T_{\text{min}}$ and m_{EP} or m_{RP} is a fraction or has a fraction component.

The reasons for introducing these two additional new models are to demonstrate that experimental temperature–viscosity data within a particular temperature range can be effectively described by several two-parameter models at the same degree

of fit, and to re-emphasize that a good fit by itself is insufficient to establish a model's physical interpretation, see below.

Estimating the parameters of temperature–viscosity models

Estimating the described temperature–viscosity models' parameters can be done in two principal ways: by direct calculation from two or three experimental viscosity measurements obtained at two or three constant temperatures, and by regression using experimental viscosity measurements at several chosen temperatures. The mathematical calculation procedures themselves are the same for the Newtonian viscosity of Newtonian liquid foods and the apparent viscosity on non-Newtonian ones, except that in the latter all the measurements ought to be made at the same specified constant shear rate or rates. Also, all that follows refers to *dynamic viscosities*, i.e., to viscosities determined at a pertinent temperature range *without* adjustment for the accompanying changes in density. The described models are most likely also applicable to *kinematic viscosities* ($\mu_{\text{kinematic}} = \mu_{\text{dynamic}}/\rho$ where ρ is the density), albeit with different parameter magnitudes. This is because the density changes in liquid foods at pertinent temperatures are much smaller relative to those in viscosity. The mention of "pertinent temperatures" is needed here because all the models, regardless of type, will most probably fail at and close to the boiling or freezing point, for example, or at temperatures high enough to induce significant chemical changes.

Direct calculation

According to the original Arrhenius model, experimental determination of a fluid's viscosities, $\mu(T_1)$ and $\mu(T_2)$, at any two chosen absolute temperatures T_1 and T_2, in a pertinent range, enables to extract the term E_a/R from the viscosities ratio, i.e.,

$$\frac{E_a}{R} = \frac{\text{Ln}\left[\frac{\mu(T1)}{\mu(T2)}\right]}{\frac{1}{T_1} - \frac{1}{T_2}}. \tag{12}$$

Once E_a/R has been calculated in this way, it can be inserted back into Equation (1), with either T_1 or T_2 (in K) serving as the reference temperature, and used to estimate any third viscosity $\mu(T_3)$ at a chosen third absolute temperature T_3 in the pertinent temperature range. The calculated $\mu(T_3)$ value can then be compared to the actual value thereby testing the accuracy of the model's predictions. Similarly, Equation (1) with the so calculated E_a/R inserted can be used to reconstruct and plot a temperature–viscosity curve from which viscosity at any desired temperature can be estimated. Or alternatively, when superimposed on additional data if available, the reconstructed curve will reveal how close the model predicts them. Where there is a perfect match between the model's predictions and the actual data, the choice of T_1 and T_2 would be immaterial. However, when the model's fit is not perfect, i.e., the Arrhenius equation only provides a rough approximation, different pairs of temperature will show different degrees of discrepancy.

Thus, when using the original Arrhenius equation as a model, the direct calculation method is much safer for interpolation within a narrow temperature range between the chosen two points than for extrapolation outside this range, see below.

When the model's equation has two adjustable parameters, i.e., the modified Arrhenius equation (Equation (6)), WLF model (Equation (2)), expanded exponential model (Equation (9)), etc., the direct extraction of their parameters can be done by the FindRoot function of Mathematica® (Wolfram Research, Champaign IL, USA), the program used in this work, or by similar equation-solving programs in other commercial mathematical software. The numerical solution, however, requires a triplet of experimental temperature/viscosity data, i.e., $\mu(T_1)$, $\mu(T_2)$, and $\mu(T_3)$ determined at temperatures T_1, T_2, and T_3, respectively, to be definitive. The same triplets can also be used to extract the VTF model's three-parameters.

In the case of the modified Arrhenius model, the simultaneous equations to be solved numerically are:

$$\text{Ln}\left[\frac{\mu(T_1)}{\mu_{T_{\text{ref}}}}\right] = a\left(\frac{1}{T_1 + b} - \frac{1}{T_{\text{ref}} + b}\right) \tag{13a}$$

$$\text{Ln}\left[\frac{\mu(T_2)}{\mu_{T_{\text{ref}}}}\right] = a\left(\frac{1}{T_2 + b} - \frac{1}{T_{\text{ref}} + b}\right) \tag{13b}$$

$$\text{Ln}\left[\frac{\mu(T_3)}{\mu_{T_{\text{ref}}}}\right] = a\left(\frac{1}{T_3 + b} - \frac{1}{T_{\text{ref}} + b}\right), \tag{13c}$$

where the three unknowns are $\mu_{T_{\text{ref}}}$, a, and b. Notice that the chosen reference temperature, T_{ref}, can but need not be one of the three temperatures. If it is, then its corresponding $\mu(T)$ will be the $\mu_{T_{\text{ref}}}$. However, an attempt to reduce the number of equations to two by doing this, i.e., by treating one of the two temperatures as T_{ref} and the corresponding viscosity as $\mu_{T_{\text{ref}}}$ may result in an indefinite solution.

This also applies to the WLF and the other models in which cases the three simultaneous equations are, respectively:

$$\text{Log}_{10}\left[\frac{\mu(T_1)}{\mu_{T_{\text{ref}}}}\right] = -\frac{C_1(T_1 - T_{\text{ref}})}{C_2 + (T_1 - T_{\text{ref}})} \tag{14a}$$

$$\text{Log}_{10}\left[\frac{\mu(T_2)}{\mu_{T_{\text{ref}}}}\right] = -\frac{C_1(T_2 - T_{\text{ref}})}{C_2 + (T_2 - T_{\text{ref}})} \tag{14b}$$

$$\text{Log}_{10}\left[\frac{\mu(T_3)}{\mu_{T_{\text{ref}}}}\right] = -\frac{C_1(T_3 - T_{\text{ref}})}{C_2 + (T_3 - T_{\text{ref}})}, \tag{14c}$$

where the three unknowns are $\mu_{T_{\text{ref}}}$, C_1, and C_2, and

$$\text{Ln}\left[\frac{\mu(T_1)}{\mu_{T_{\text{ref}}}}\right] = c_1(T_{\text{ref}} - T_1) + c_2(T_{\text{ref}} - T_1)^2 \tag{15a}$$

$$\text{Ln}\left[\frac{\mu(T_2)}{\mu_{T_{\text{ref}}}}\right] = c_1(T_{\text{ref}} - T_2) + c_2(T_{\text{ref}} - T_2)^2 \tag{15b}$$

$$\text{Ln}\left[\frac{\mu(T_3)}{\mu_{T_{\text{ref}}}}\right] = c_1\ (T_{\text{ref}} - T_3) + c_2(T_{\text{ref}} - T_3)^2, \tag{15c}$$

where the three unknowns are $\mu_{T_{\text{ref}}}$, c_1, and c_2.

The VTF's (or VFT's) three parameters can be extracted by solving the three simultaneous equations:

$$\text{Ln}[\mu(T_1)] = A_{\text{VTF}} + \frac{B_{\text{VTF}}}{T_1 - T_0} \tag{16a}$$

$$\text{Ln}[\mu(T_2)] = A_{\text{VTF}} + \frac{B_{\text{VTF}}}{T_2 - T_0} \tag{16b}$$

$$\text{Ln}[\mu(T_3)] = A_{\text{VTF}} + \frac{B_{\text{VTF}}}{T_3 - T_0}, \tag{16c}$$

where the three unknowns are A_{VTF}, B_{VTF}, and T_0.

Similar equation triplets can be written for other two alternative models, Equations (10) and (11), see below.

Regression

Where several temperature–viscosity data points are available, the various models' parameters can be estimated by regression. In what follows this was done using Mathematica's NonliearModelFit function where the model was expressed in the explicit form of $\mu(T)$ vs. T and so were the data, i.e., they were entered without logarithmic transformation of the reported experimental viscosities. This and similar regression programs not only estimate the model's parameters but also provide statistical goodness-of-fit indices for comparison, notably the regression coefficient r^2. As before, the sought regression parameters are E_a/R of the original Arrhenius equation, $\mu_{T_{\text{ref}}}$, a, and b of the modified Arrhenius model, C_1 and C_2 of the WLF model, the A_{VTF}, B_{VTF}, and T_0 of the VTF model, c_1 and c_2 of the expanded exponential model, etc. If in testing the modified Arrhenius, and the other alternative models, one of the temperatures is chosen as T_{ref} and the corresponding viscosity as $\mu_{T_{\text{ref}}}$, the number of sought regression parameters is reduced to two, i.e., a and b, C_1 and C_2 or c_1 and c_2, etc. Doing this, however, may lower the fit's r^2 slightly and hence is not recommended. As before, this issue does not arise with the VTF model, which has three adjustable parameters that do not include $\mu_{T_{\text{ref}}}$.

Initial guesses

Both the numerical solution of simultaneous nonlinear equations and nonlinear regression require close enough initial guesses of the sought parameters for the procedure to render realistic values and sometimes any values at all. The value of $\mu_{T_{\text{ref}}}$ or $\mu_{T_{\text{min}}}$, where it appears in the model's equation is either known or can be easily estimated from the data at hand by interpolation or extrapolation. The other parameters' initial values can be obtained by trial and error, or, more effectively, with a special interactive program. For a chosen model equation, the user attempts to pass a matching curve through three experimental $\mu(T)$ vs. T data points by manually moving sliders on the screen. When a visual match is obtained, the corresponding sliders' positions serve as the sought initial guesses for the numerical procedure that follows, i.e., the simultaneous equations solution or for nonlinear regression using an entire dataset. Three examples of this method's application, showing actual matches to experimental data, are given in Figures 1–3. The models used to generate them were the modified Arrhenius

equation (Equation (6)), the expanded exponential model (Equation (9)), and the reciprocal-power-law model (Equation (11)). The three figures were created with Mathematica's Manipulate function, and the author will be glad to share the program's code with interested readers upon request. Similar programs can be written for the WLF and VTF models, if desired, although their parameters can be calculated directly from the values of a and b obtained for the modified Arrhenius equation using the formulas given in the Appendix.

Comparison of the models' performance

A list of the compared models, their respective equations, and the name and number of their adjusted parameters is given in Table 1. The database for the comparison are numerical temperature–dynamic viscosity data of a 40% sucrose solution in the range of 0 to 95°C obtained from *The Engineering ToolBox* on the web (http://www.engineeringtoolbox.com/sugar-solutions-dynamic-viscosity-d_1895.html). The soybean oil data in the range of 35 to 180°C were obtained from Fasina and Colley (2008), and those on the 70°Bx clarified pear juice concentrate in the range of 5 to 60°C from Ibraz et al. (1987). The viscosity units are those originally reported; mPa s for the 40% sucrose solution and soybean oil, and Pa s for the pear juice concentrate. The three datasets cover different temperature ranges and viscosity levels, and the sole purpose of their choice has been to compare their fit by the various temperature–viscosity models listed in the table.

Calculation of the original Arrhenius equation's parameters by the two-point method and its modified version by the three-point method

Figure 4 shows a comparison of the fits of the traditional Arrhenius equation (Equation (1)) when E_a/R has been calculated from two experimental data points using Equation (12) (dotted curves), and the fit of the modified Arrhenius equation (Equation (6)) where $\mu_{T_{\text{ref}}}$, a, and b have been calculated from three experimental data points by solving the corresponding simultaneous Equations (13a), (13b), and (13c) (dashed curve).

The figure shows that in the soybean oil case, the two methods rendered parameters that resulted in the same practically perfect fit to the entire dataset. This kind of observation is expected from ideal Arrhenius behavior, in which case the choice of the two points has no effect on the results. This has been verified by calculating the soybean oil's E_a/R from a different pair of points. The cases of the 40% sucrose solution and 70°Bx pear juice concentrate are different. In both, the three-point method has resulted in a substantially improved fit to their entire datasets, i.e., to a considerable better prediction of their viscosities at temperatures not used in the parameter calculation.

Comparison of the modified Arrhenius model's fit obtained by the three-points method and by regression

Examples of the modified Arrhenius model's fit, and hence that of the WLF and VTF models as well, when its parameters are calculated by the three-point method (Equations (13a), (13b), and (13c)) and by nonlinear regression with Equation (6) as
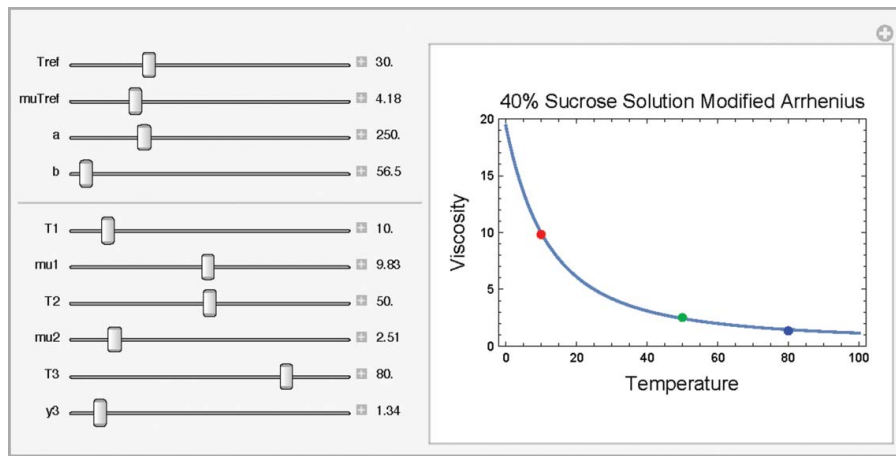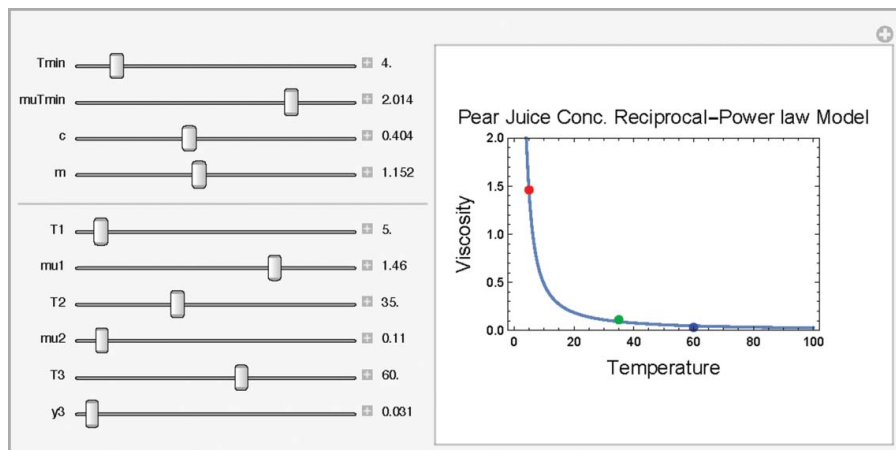
Figure 1. Screen display of an interactive program to estimate the parameters of the modified Arrhenius model (Equation (6)) from three experimental temperature–viscosity data points. The *muTref, a*, and *b* sliders' positions when a visual match between the entered points and reconstructed curve is obtained are the corresponding parameters' estimates.
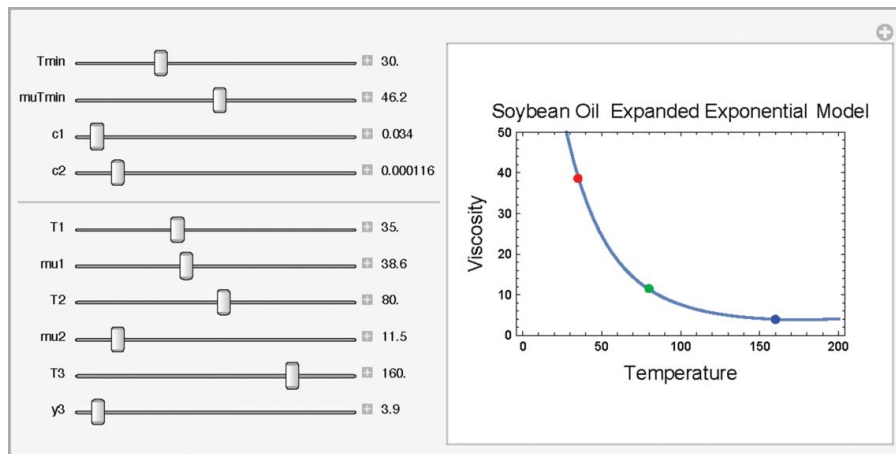
Figure 2. Screen display of an interactive program to estimate the parameters of the expanded exponential model (Equation (9)) from three experimental temperature-viscosity data points. The *muTmin, c_1*, and *c_2* sliders' positions when a visual match between the entered points and reconstructed curve is obtained are the corresponding parameters' estimates.

the model are given in Figure 5. As expected, the fit obtained by regression is better than that obtained from three-point only. However, the differences are fairly small as judged by informal criteria, and one can argue that they are practically insignificant if the reconstructed curve obtained by the three-point method is only used for interpolation and not for extrapolation. This strengthens the view that when one opts for the three-point method, the chosen points should cover the entire expected

Figure 3. Screen display of an interactive program to estimate the parameters of the reciprocal-power law model (Equation (11)) from three experimental temperature–viscosity data points. The *muTmin, c*, and *m* sliders' positions when a visual match between the entered points and reconstructed curve is obtained are the corresponding parameters' estimates.

Table 1. List of the compared temperature–viscosity models.

Model	Equation no.	No. of theoretically adjustable parameters	Parameters
Original Arrhenius	1	1[a]	E_a (or E_a/R)
Modified Arrhenius[b]	6	2	a, b
WLF[b]	2	2	C_1, C_2
VTF (or VFT)[b]	3	3	A_{VTF}, B_{VTF}, T_0
Expanded exponential	9	2	c_1, c_2
Exponential-power law	10	2	c_{EP}, m_{EP}
Reciprocal-power law	11	2	c_{RP}, m_{RP}

[a]Because the temperature conversion from °C to K adds a constant ("nuisance factor") the number of the equation's adjustable parameters is not strictly one but at the same time it is not two either.
[b]The modified Arrhenius, WLF, and VTF equations are the same model temperature–viscosity model written in three different ways. The formulas to convert their parameters are listed in the Appendix.

temperature range of the model's application. The tradeoff between the effort to determine the entire temperature–viscosity curve experimentally to provide a sufficient number of points for regression and the potential loss of accuracy that the three-point method might cause is a logistic issue to be resolved on a case-by-case basis.
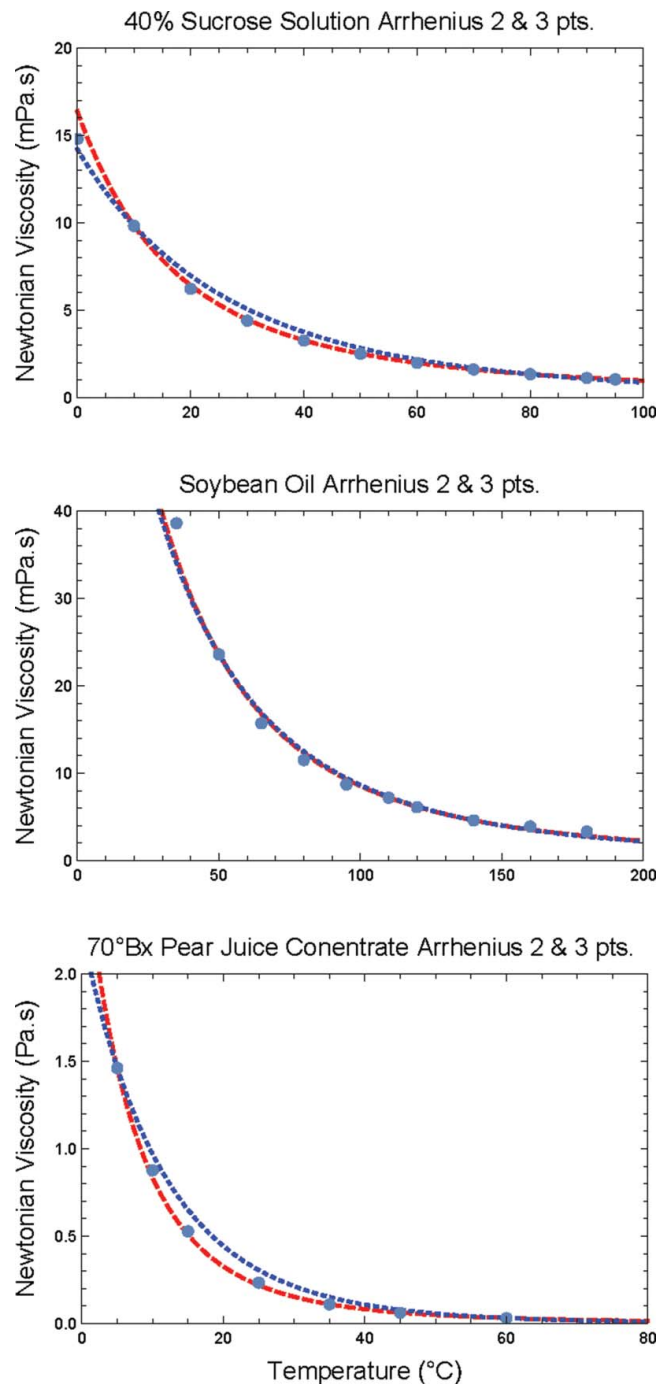
Comparison of the four non-Arrhenius models' fit obtained by regression

Examples of the actual fit of the exponential-power-law, reciprocal-power-law, and expanded exponential models are given in Figure 6. Visually, the fitted curves are almost totally indistinguishable from those of the modified Arrhenius and hence from those produced by the WLF and VTF models shown in Figure 5. The regression coefficients, r^2's, of all four non-Arrhenius models' fits to the entire datasets of the 40% sucrose solution, soybean oil, and 70°Bx pear juice concentrate are listed in Table 2. As expected from the observation that the modified Arrhenius, WLF, and VTF equations are three alternative ways to write the same temperature–viscosity model, their r^2's are indeed exactly the same as shown in the table. Although the entries in the table display only six digits after the decimal, one can show that the identity in the r^2 values continues indefinitely.

As shown in Table 2, the regression coefficients of the four non-Arrhenius models were very high. Among the 12 pertinent r^2 entries the lowest is $r^2 = 0.9988$, five are $r^2 > 0.999$ and six are $r^2 > 0.9999$. Only the hybrid reciprocal-power-law model (Equation (11)) has $r^2 > 0.9999$ in all three liquids and only the exponential-power-law model (Equation (10)) has none. However, because only three datasets have been used for the comparison, the interpretation of this observation and whether it has any practical implications remains unclear.

Concluding remarks

Analysis shows that of the six non-Arrhenius temperature–viscosity models examined three, the modified Arrhenius, WLF and VTF equations, are the very same model. The first, however, can be viewed as an Arrhenius type model where the reference point is not the standard 0 K but an adjustable parameter b representing a higher temperature. Whether the observed magnitude of b has a physical explanation or whether it is merely an artificial device to
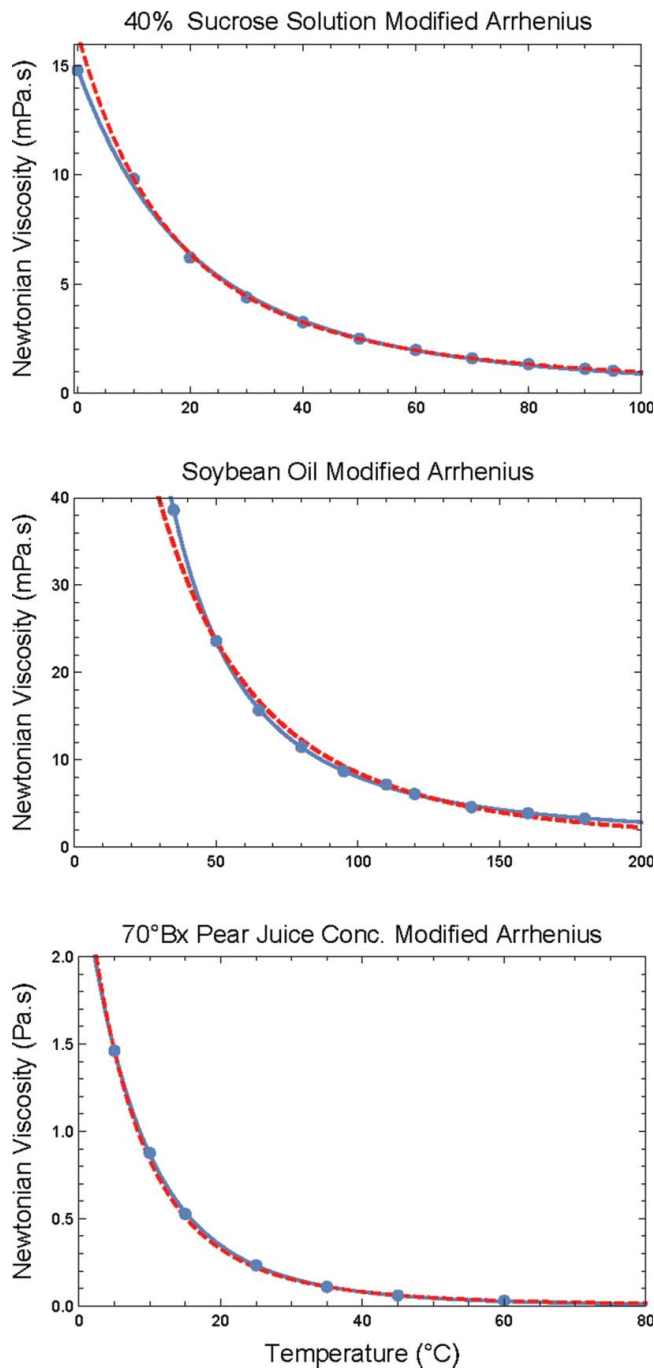

Figure 4. Comparison of the fit of the original Arrhenius equation to reported temperature–viscosity data obtained by the two-point method (Equation (12))—dotted curves, and that of the modified Arrhenius model obtained by the three-point method (Equations (13a), (13b), and (13c))—dashed curves.

improve the Arrhenius model's fit is unclear at this point. However, if the parameters of the WLF or VTF equation have physical interpretation, so do the modified Arrhenius model's a and b. With the introduced modification to the Arrhenius model's formulation and by replacing the traditional E_a/R by a having a temperature dimension and unit, the need to refer to a "mole" where it is difficult to define is eliminated. Whether in food applications of the original Arrhenius equation E_a/R should be replaced by a (in °C or K) is a possibility that should be at least considered.
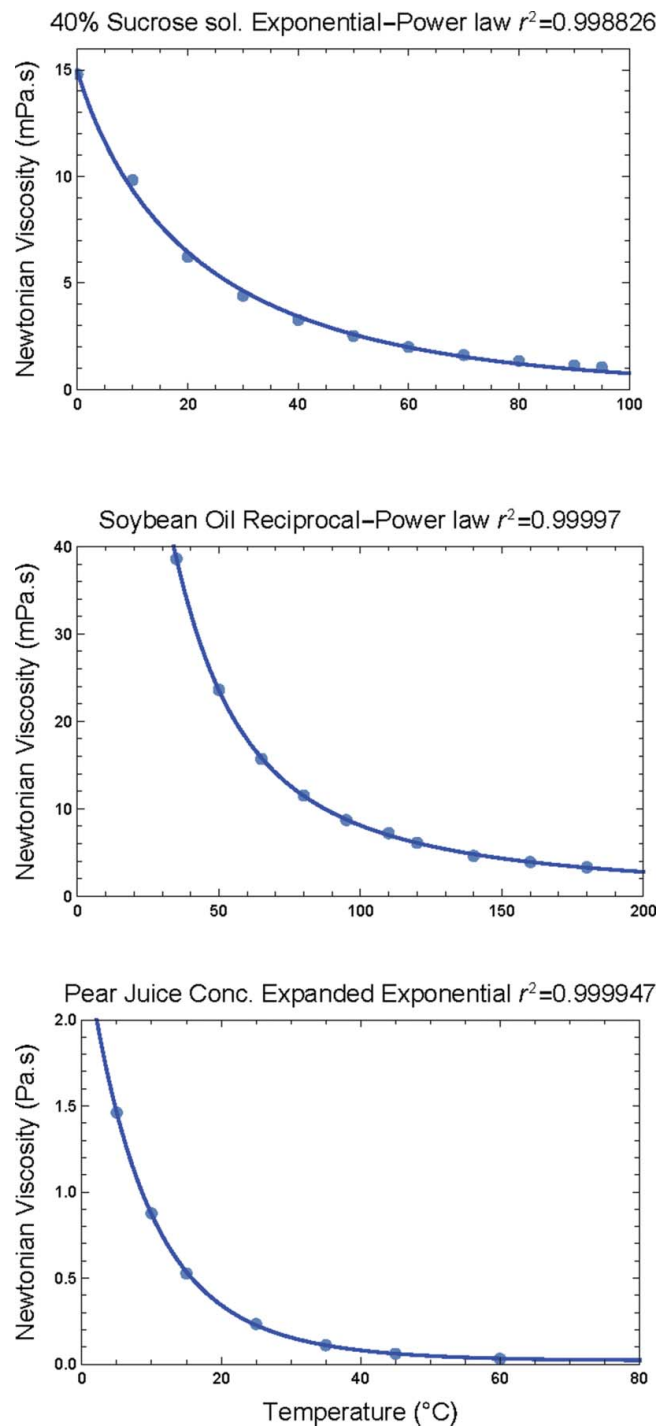
As expected, the six (actually four) "non-Arrhenius" models all have a superior fit to experimental data in comparison to

Figure 5. Comparison of the fit of the modified Arrhenius model to reported temperature–viscosity data obtained by the three-point method (Equations (13a), (13b), and (13c))—dashed curves, and by nonlinear regression—solid curves. Notice that exactly the same curves will be produced when using the WLF and VTF models.

Figure 6. The fit of the exponential-power-law model (Equation (10)) to reported temperature–viscosity data of a 40% sucrose solution (top), that of the reciprocal-power-law model (Equation (11)) to soybean oil (middle), and that of the expanded exponential model (Equation (9)) to 70°Bx pear juice concentrate (bottom).

that of the original Arrhenius equation, albeit at the expense of an additional adjustable parameter. The differences, however, as judged by the magnitude of the corresponding r^2's do not seem dramatic. At least visually, the differences between temperature–viscosity curves reconstructed with parameters calculated by the three-point method are not very different from those where the parameters were obtained by regression. Also, all the examined models are applicable only within a limited temperature range determined by their mathematical formulation and physical considerations. Therefore, they all, including the original Arrhenius equation and regardless of how their

parameters have been calculated, are safer when used to estimate viscosities by interpolation than predict them by extrapolation.

Acknowledgment

Table 2. Comparison of the regression coefficients of various temperature–viscosity models to reported experimental data (r^2 of the fit with three adjustable parameters).

Model	Equation no.	40% Sucrose solution (0–95°C)	Soybean oil (35–180°C)	70°Bx pear juice conc. (5–60°C)
Original Arrhenius[a]	1	0.998427	0.996843	0.999506
Modified Arrhenius[b]	6	**0.999529**	**0.999947**	**0.999935**
WLF[b]	2	**0.999529**	**0.999947**	**0.999935**
VTF (or VFT)[b]	3	**0.999529**	**0.999947**	**0.999935**
Expanded exponential	9	0.999674	0.999257	0.999947
Exponential-power law	10	0.998826	0.999799	0.999831
Reciprocal-power law	11	0.999910	0.999957	0.999956

[a]Fitted with only two adjustable parameters, namely, $\mu_{T_{ref}}$ and E_a/R.
[b]Notice that because the modified Arrhenius, WLF, and VTF equations are three alternative versions of the same model, see the Appendix, their r^2's in each liquid must be the same.

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Appendix

1. The equality of the VTF and WLF equations:

$$\mathrm{Ln}\left[\frac{\mu(T)}{\mu_{T_{ref}}}\right] = A + \frac{B}{T - T_0} - A - \frac{B}{T_{ref} - T_0}$$

$$= B\left(\frac{1}{T - T_0} - \frac{1}{T_{ref} - T_0}\right)$$

where $C_1 = \frac{B\mathrm{Log}_{10}e}{T_{ref} - T_0}$ and $C_2 = T_{ref} - T_0$.

2. The equality of the modified Arrhenius and WLF equations:
where $C_1 = \frac{a}{\mathrm{Ln}[10](T_{ref} + b)}$ and $C_2 = T_{ref} + b$.

3. The equality of the modified Arrhenius and VTF equations:

$$\mathrm{Ln}[\mu(T)] = \mathrm{Ln}[\mu(T_{ref})] + \frac{a}{T + b} - \frac{a}{T_{ref} + b}$$

$$= \mathrm{Ln}[\mu(T_{ref})] - \frac{a}{T_{ref} + b} + \frac{a}{T + b}$$

$$= A + \frac{B}{T - T_0},$$

where $A = \mathrm{Ln}[\mu(T_{ref})] - \frac{a}{T_{ref} + b}$, $B = a$, and $T_0 = -b$.

Conclusion: The modified Arrhenius, WLF, and VTF equations are three alternative ways to write the same temperature–viscosity model.