A Comprehensive Expression for Temperature Dependence of Liquid Viscosity

by

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(Received: June 8, 1987)

Abstract

A simple empirical expression for temperature dependence of liquid viscosity, which carries two adjustable parameters and includes a glass transition temperature, \(T_g\), and the liquid viscosity \(\eta_k\) at \(T_g\), has been proposed in the form:

\[
\log \left( \frac{\eta}{\eta_k} \right) = A [\exp \left( B(T_g - T)/T \right) - 1]
\]

This expression has been applied to 14 liquids including polymeric materials. The mean values of \(A\) and \(B\) for 11 substances are found to be 15.29 ± 1.04 and 6.47 ± 1.13, respectively. The Andrade equation and the Williams-Landel-Ferry equation for liquid viscosity can be derived analytically from the proposed equation with reasonable approximation.

Key words: Viscosity / Glass transition temperature / Andrade equation / WLF equation

INTRODUCTION

Liquid viscosity is generally known to decrease in magnitude when liquid temperature is increased. In 1930 Andrade¹ expressed this temperature dependence in the following form,

\[
\ln \eta = C + D / (RT)
\]

where \(\eta\) is the liquid viscosity at \(T\) K, \(R\) the gas constant, \(C\) and \(D\) are constants for individual liquids, \(D\) being the activation enthalpy. Equation (1) was interpreted molecularly by Eyring et al.²,³ and Weymann⁴,⁵ in terms of the rate process theory; and these ideas were later developed toward the significant structure theory of liquids.⁶

There are many examples which demonstrate that equation (1) is inadequate especially at lower temperatures and for a wide range of viscosity and temperature. Particularly conspicuous is the behavior of molten polymeric substances around their glass transition regions. Plots of \(\ln \eta\) vs. \(1/T\) are invariably non-linear so that constant activation enthalpies of melt viscosity are untenable.

In 1951, Doolittle⁷ proposed that the temperature dependence of viscosity of n-paraffins can be explained in terms of the free volume concept. This is akin to what Batchinski⁸ considered earlier to describe the temperature dependence of liquid viscosity. Liquids are composed of molecules of finite size having free volume (i.e., free spaces between molecules). Liquid viscosity decreases with increasing temperature as the result of reduced friction between molecules, arising from reduced intermolecular interaction with increasing free volume. The temperature dependence of liquid viscosity is inherent in the change of liquid volume.

Based upon Doolittle's proposal, Williams-Landel-Ferry (WLF)⁹ proposed an empirical viscosity relationship now called the WLF equation. This expression is:

\[
\log \left( \frac{\eta}{\eta_k} \right) = -C_1 \frac{(T - T_g)}{(C_2 + (T - T_g))}
\]

where \(T_g\) is the glass transition temperature, employed here as a reference temperature, \(\eta_k\) is the viscosity at \(T_g\), \(C_1\) and \(C_2\) are found to be constants for many liquids and polymeric materials. Usually \(C_1\) and \(C_2\) have values of 17.44 and 51.6, respectively. Cohen and Turnbull¹⁰ derived this type of
equation theoretically on the basis of the liquid cage model of Lenard-Jones and Devonshire\cite{11}. The WLF equation is substantially the same as the expression

\[ \ln \left( \eta / \eta_0 \right) \approx \frac{1}{T - T_0} \]  

employed much earlier by Vogel\cite{12}, Fulcher\cite{13}, Tamman-Hesse\cite{14} (designated as the VFTH equation). In equation (3), \( T_0 \) is assumed to be a reference temperature related to \( T_\text{g} \). Alternatively, Adam and Gibbs\cite{15} have shown that a similar expression to equation (2) may also be derived in terms of a configurational entropy change in polymeric materials.

It must be emphasized that the temperature dependence of liquid viscosity over a wide temperature span and extensive range of viscosity cannot be described solely by equation (1) or (2). Ordinarily, the equation (1) describes viscosity data in the temperature range well above \( T_\text{g} \) whereas equation (2) is limited to the temperature interval between \( T_\text{g} \) and \( T_\text{g} + 100 \text{ K} \). In an effort to describe the viscosity data in a wider temperature range, Macedo and Litovitz\cite{16} combined equation (1) and equation (2), and thus proposed the “hybrid” equation; however, Brummer\cite{17} criticized their idea toward the point that the assumed constant activation energy in the “hybrid” equation is seriously flawed. In fact this equation is inapplicable to the viscosity data of tri-\( \alpha \)-naphthylbenzene (T\( \alpha \)NB) since least-squares curve fitting to the “hybrid equation” gave rise to anegative activation energy\cite{18}.

In the past decade, Magill and Li\cite{19} or Breitling and Magill\cite{20} proposed the new expressions with adjustable parameters for the temperature dependence of liquid viscosity. Although these equations can express viscosity as a function of temperature over a wide range, they still remain to be correlated with the Andrade equation or the WLF equation analytically. Litt\cite{21} has also shown that the viscosity change over a wide interval, may be described on the basis of a free volume theory by Bueche\cite{22}.

A knowledge of viscosity-temperature relationships is important for technological applications. Equations for this purpose should contain the minimum numbers of adjustable parameters. Besides they ought to be applicable over a wide temperature and viscosity range. In the present study, we propose a novel expression for temperature dependence of viscosity and examine this expression in relation to other models mentioned above.

A NEW EXPRESSION FOR TEMPERATURE DEPENDENCE OF LIQUID VISCOSITY

The expression we propose here is the following form:

\[ \log \left( \eta / \eta_0 \right) = A \exp \left[ B \left( T_\text{g} - T \right) / T \right] - 1 \]  

where both \( A \) and \( B \) are constants related to individual liquids. If we take the viewpoint that the glass transition is the isoviscous state\cite{23} then

\[ T_\text{g} = 10^{11} \text{ [poise]} \]  

thus the parameters in equation (4) are reduced to only \( A \) and \( B \). To determine the values of \( A \) and \( B \), we selected 14 liquids with viscosities measured over a wide temperature range, applying the non-linear least-square fit method by a personal computer. The viscosity data utilized here have different accuracies due in part to various methods of viscosity measurement used.

The typical results of curve fittings are shown in Fig. 1, 2, and 3. The values of \( A \) and \( B \) thus determined are summarized in Table I. The average values, except for the materials with asterisks, are

\[ A = 15.29 \pm 1.04 \]  

and

\[ B = 6.47 \pm 1.13 \],

Thus these fitting values seem to be reasonably constant for the various materials examined in this paper.

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![Fig. 1 Curve fitting results of viscosity changes to equation (4). The symbols shown in the figure are: C, di-n-butylphthalate\cite{24}; A, tri-\( \alpha \)-naphthylbenzene\cite{25,26}; D, \( \alpha \)-phenyl-o-cresol\cite{27,28}. Viscosity is indicated in poise.](image1)

![Fig. 2 Curve fitting results of viscosity changes to equation (4). The symbols shown in the figure are: C, glucose\cite{29}; A, KNO\textsubscript{3}-Ca(NO\textsubscript{3})\textsubscript{2}\cite{30,31}; D, o-terphenyl\cite{32,33}. Viscosity is indicated in poise.](image2)
RELATIONSHIP BETWEEN THE NEW EXPRESSION AND OTHER
EXPRESSIONS

a) Correlation to the WLF equation
When the experimental temperatures are close to the glass transition temperature, we can approximate \((T - T_g)/T < 1\); then equation (4) can be reduced to the following form

\[
\log\left(\frac{\eta}{\eta_0}\right) = A\text{exp}\left(\frac{B(T - T_g)}{T}\right)/\exp\left(\frac{-B}{T}\right)
\]

where \(\exp(-B) = B'\).

Thus equation (6) also becomes equivalent to the WLF equation when \(A = C_1\) and \(T_g/B = C_2\). As already mentioned, the value of \(A\) is close to that of 17.44. If we take \(T_r = -323 \text{ K (}50\text{ °C)}\), then \(T_r/B = 50\) which is also close to the value of \(C_2\). At any rate, from these discussions, equivalency of equation (6) and the WLF expression is apparent.

b) Correlation to the Andrade equation
When temperatures are well above \(T_g\), e.g., \(B(T_g/T) < 1\), equation (4) becomes:

\[
\log\left(\frac{\eta}{\eta_0}\right) = A\text{exp}\left(B(T_g/T)\right)/\text{exp}\left(-B\right) - 1
\]

where \(\text{exp}(-B) = B'\).

The equation (8) takes the form of the Andrade equation. Therefore, equation (4) is also considered to contain equation (1). For these reasons it seems more universal or at least more widely applicable than the WLF expression.

c) Comparison between other viscosity equations
Brief comments on other viscosity equations will be appropriate at this point. The Magill-Li (M-L) equation may

Table I. Estimated values of parameters \(A\) and \(B\) by use of equation (4).

<table>
<thead>
<tr>
<th>No</th>
<th>Materials</th>
<th>(T_g) (K)</th>
<th>Temperature range (K)</th>
<th>(A)</th>
<th>(B)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>di-n-Butylphalate</td>
<td>174</td>
<td>179.5~370.1</td>
<td>15.34</td>
<td>5.49</td>
<td>10^-1</td>
</tr>
<tr>
<td>2</td>
<td>d-Sorbitol</td>
<td>258</td>
<td>264.4~365.9</td>
<td>14.11</td>
<td>5.67</td>
<td>5x10^-3</td>
</tr>
<tr>
<td>3</td>
<td>Glycerin*</td>
<td>182</td>
<td>~473</td>
<td>19.68</td>
<td>2.44</td>
<td>10^-2</td>
</tr>
<tr>
<td>4</td>
<td>Glucose</td>
<td>299</td>
<td>295.1~418.1</td>
<td>14.87</td>
<td>6.21</td>
<td>7x10^-3</td>
</tr>
<tr>
<td>5</td>
<td>2-Methylpentane*</td>
<td>79.8</td>
<td>80.5~96.5</td>
<td>21.71</td>
<td>2.54</td>
<td>5x10^-2</td>
</tr>
<tr>
<td>6</td>
<td>o-Terphenyl</td>
<td>240</td>
<td>239.4~416.5</td>
<td>16.18</td>
<td>6.46</td>
<td>5x10^-2</td>
</tr>
<tr>
<td>7</td>
<td>tri-(\alpha)-naphthylbenzene</td>
<td>336</td>
<td>332.4~680.1</td>
<td>16.00</td>
<td>5.96</td>
<td>7x10^-2</td>
</tr>
<tr>
<td>8</td>
<td>Phenylsalicylate</td>
<td>215</td>
<td>213.2~333.2</td>
<td>15.65</td>
<td>7.00</td>
<td>10^-1</td>
</tr>
<tr>
<td>9</td>
<td>(\alpha)-Phenyl-o-cresol</td>
<td>212</td>
<td>207.9~414.7</td>
<td>15.39</td>
<td>6.99</td>
<td>10^-1</td>
</tr>
<tr>
<td>10</td>
<td>Isopropylbenzene</td>
<td>128</td>
<td>130~303.2</td>
<td>15.44</td>
<td>6.77</td>
<td>1.0</td>
</tr>
<tr>
<td>11</td>
<td>n-Butylbenzene</td>
<td>128</td>
<td>136~303.2</td>
<td>15.48</td>
<td>5.97</td>
<td>10^-2</td>
</tr>
<tr>
<td>12</td>
<td>KNO(_3)-Ca(NO(_3))(_2)</td>
<td>334</td>
<td>330.2~473.4</td>
<td>15.04</td>
<td>7.75</td>
<td>3x10^-2</td>
</tr>
<tr>
<td>13</td>
<td>Polystyrene (low MW)</td>
<td>307</td>
<td>310.6~453.1</td>
<td>14.70</td>
<td>6.29</td>
<td>10^-1</td>
</tr>
<tr>
<td>14</td>
<td>Polyisobutylene*</td>
<td>205</td>
<td>190.4~232.9</td>
<td>13.04</td>
<td>3.25</td>
<td>2.0</td>
</tr>
</tbody>
</table>

*) The \(A\) and \(B\) values of these materials had been removed when average operation was conducted.
See text.
be written as:

\[ \ln \left( \frac{\eta}{\eta_r} \right) = A_1 \left[ \exp \left( B_1 T_g/T \right) - \exp \left( \frac{1}{1 + \phi} \right) \right] \]  

where \( \eta/\eta_r \) is the reduced viscosity with a reference value of \( \eta_r \), and the parameters \( A_1, B_1 \) and \( \phi \) are 0.011, 7.19 and 0.24, respectively, being constant for all the materials examined. Alternatively, the Breitling-Magill (B-M) equation \(^{20}\) may be expressed as follows,

\[ \ln \left( \frac{\eta}{\eta_s} \right) = A_2 \left[ \frac{x-1}{x+\phi} \exp \left( \frac{B_2}{x+\phi} \right) \right] \]  

In this relationship, \( A_2, B_2, \) and \( \phi \) are 2.68, 0.432 and 0.238, respectively. The variable of reduced temperature \( x = T/T_g \) for a given material, and \( \eta_s \) is its individual standard viscosity value. Although these equations provide a reasonable representation of experimental data as already shown in references \(^{19, 20}\), they do not seem to be equivalent analytically. Equation (6) or (6a) is probably relatable to the M-L or the B-M equations as expected from their similar functional forms. Note, however, that only equation (4) provides an acceptable representation of the experimental results for many materials, and also its equivalency to the WLF relationship can be realized analytically. Equations (9) and (10) cannot be related to the WLF or to the Andrade type relationship.

**CONCLUSION**

It has been found that the novel viscosity-temperature expression proposed in this paper adequately describes the viscosity-temperature relation of molecular and other liquids including polymeric substances. Of course, more viscosity data for other substances should be tested using this expression in future. Uttracki \(^{20}\) has suggested an equation somewhat similar to ours but containing several adjustable parameters. At any rate, his expression appears to be less widely applicable to many types of liquids. A theoretical basis for our expression is now being sought in our laboratory.

The authors express their gratitude to Professor D.J. Plazek of University of Pittsburgh, for helpful discussion and for providing some of his experimental data. They also thank Mrs. M. Inoue and Mr. K. Saito of Yamagata University for assistance with tabulation of viscosity-temperature data.

(This paper was presented at the 33th Japan Rheology Conference, Yonezawa, in 1985)

**REFERENCES**


