

WLF 점도식의 반응속도론에 의한 도출

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요 약

“Significant liquid structure”의 이론과 반응 속도 이론을 이용 WLF 점도식 꼴을 도출하였다. 반 실험적 WLF 점도식 내 실험 Parameter 와 도출된 이론식 중의 해당된 항을 비교 검토하였다.

Derivation of the WLF Equation from the Theory of Rate Process*

by

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ABSTRACT

The WLF equation is derived from the theory of rate processes in conjunction with the theory of liquids of significant structures. The empirical parameters in the WLF equation are discussed and compared with the corresponding quantities in the derived equation.

1. INTRODUCTION

In the past years, many studies were published on the temperature dependence of viscosities for glass forming liquids.⁽¹⁻⁷⁾ Among them, the successful semiempirical relation, which is often called the WLF equation after the authors' name, Williams, Landel, and Ferry,⁽²⁾ is represented as

$$\ln(\eta_g/\eta) = 40(T - T_g) / [52 + (T - T_g)], \dots (1)$$

where η denotes the viscosity at temperature T , and the

quantities with the suffix g indicate the corresponding quantities at the glass transition. In this paper, the WLF equation is derived from the theory of rate processes,⁽⁸⁻⁹⁾ and the empirical parameters such as 40 and 52 in equation (1) are correlated with the quantities appeared in the derived equation.

2. DERIVATION OF THE WLF EQUATION

The shear viscosity equation⁽⁹⁾ developed by Ree, Ree and Eyring starting from the significant liquid-

structure concept⁽¹⁰⁻¹¹⁾ and the theory of rate processes⁽⁶⁾ has the following form:

$$\eta = \left(\frac{V_g}{V}\right)\eta_s + \left(\frac{V-V_g}{V}\right)\eta_{gas}, \quad \dots\dots\dots(2)$$

where V_g and V are the molar volumes of the solid and liquid, respectively, η_s and η_{gas} are the viscosities of the solid and gaseous states. The quantity η_{gas} which is derived from the kinetic theory⁽¹²⁾ has the form, $\eta_{gas} = (5/16d^2)(mkT/\pi)^{1/2}$, where m and d are the molecular mass and diameter, respectively. The expression for η_s is as follows:⁽²⁾

$$\eta_s = \frac{V}{V_g} \frac{(\pi mkT)^{1/2} N l_f}{2(V-V_g)\kappa} \exp\left[\frac{-a' V_g Z \varphi(a)}{(V-V_g)2kT}\right] \quad \dots\dots\dots(3)$$

Here l_f is the free distance between nearest neighbors, κ is a transmission coefficient, a' is a proportionality constant, $\varphi(a)$ is an intermolecular potential function, Z is the number of nearest neighbors, k is Boltzmann's constant, and N is Avogadro's number.

Since η_{gas} is quite small, this contribution (0 to 2%) can be neglected. Thus, introducing equation (3) into (1), one obtains

$$\eta = \frac{(\pi mkT)^{1/2} N l_f}{2(V-V_g)\kappa} \exp\left[\frac{-a' V_g Z \varphi(a)}{(V-V_g)2kT}\right] \\ = B \exp\left[\frac{a' E_s V_g}{(V-V_g)RT}\right] \quad \dots\dots\dots(4a)$$

where

$$B = \frac{(\pi mkT)^{1/2} N l_f}{2(V-V_g)\kappa}, \quad E_s = -\frac{N \varphi(a) Z}{2}$$

and E_s is the sublimation energy. Equation (4a) is represented as

$$\ln \eta = \ln B + \frac{a' E_s V_g}{(V-V_g)RT} \quad \dots\dots\dots(4b)$$

Consider the viscosities of a liquid at two different temperatures, T_1 and T_2 . From equation (4b), the following is resulted:

$$\ln \frac{\eta_1}{\eta_2} = \frac{a' E_s V_g}{R} \left[\frac{1}{(V_1-V_g)T_1} - \frac{1}{(V_2-V_g)T_2} \right] \quad \dots\dots\dots(5)$$

where it is assumed that the temperature dependence of B is very small for certain temperature ranges. Using the relation, $X_2 = X_1 + \alpha X_1(T_2 - T_1)$, where $X_i = V/V_g$ and α is the expansion coefficient for the glass-forming liquid (α_l) minus that for the glass (α_g),⁽¹³⁻¹⁵⁾ equation (5) is transformed into

$$\ln \frac{\eta_1}{\eta_2} = \frac{a' E_s}{R} \left[-\frac{1}{(X_1-1)T_1} - \frac{1}{(X_1-1) + \alpha X_1(T_2-T_1)T_2} \right] \quad \dots\dots(6)$$

Rearranging Eq. (6) and assuming $1 \gg \frac{1}{T_1 T_2}$, one obtains

$$\ln \frac{\eta_1}{\eta_2} = \frac{a' E_s}{R} \frac{1}{(X_g-1)T_g} \frac{(T_1-T_2)}{\frac{X_g-1}{\alpha X_g} + (T_1-T_2)} \quad (7)$$

where the suffix 1 was changed to g , and the quantities suffixed 2 were unsuffixed. Equation (7) is exactly equal to the WLF equation, if the following relations hold:

$$\frac{a' E_s}{R} \frac{1}{(X_g-1)T_g} \approx 40 \quad \dots\dots\dots(8)$$

$$(X_g-1)/\alpha X_g \approx 52 \quad \dots\dots\dots(9)$$

3. DISCUSSION

(1) First we consider the relation represented by equation (9).

The left-hand side of the latter is rewritten as

$$\frac{X_g-1}{\alpha X_g} = \frac{V_g-V_s}{\alpha V_g} = \frac{V_{fg}}{\alpha V_g} \quad \dots\dots\dots(10)$$

where V_{fg}/V_g is the fraction of free volume at T_g , and it was estimated as about 1/40 by many authors.

⁽¹³⁻¹⁵⁾ Recent data on polystyrene and polyisobutylene⁽¹³⁾ and polyethylene⁽¹⁴⁾ also indicate that the estimated value is substantially correct. The value of α is about $5 \times 10^{-4}/\text{deg}$ for most high polymers.⁽¹³⁻¹⁵⁾ Thus, the $V_{fg}/\alpha V_g$ becomes ≈ 52 in agreement with the WLF equation.

In equation (10), V_g is considered to be the liquid volume at T_g occupied by a mole of segments of the polymer molecule, and V_s is understood as the volume of a mole of the segments at the solid state. According to the rate theory of flow processes,⁽⁶⁾ a hole (or free volume), the size of which must at least be V_s per mole, should exist next to the segment, otherwise the jumping of the segment is unsuccessful, consequently flow does not occur. Since $V_{fg}/V_g = (V_{fg}/V_s)(V_s/V_g) = 1/40$, the value of V_{fg}/V_g becomes 1/39 because $V_g/V_s = 40/39$. Thus at T_g , the average free volume per mole of segments ($V_g - V_s$) is only 1/39 the necessary hole size (V_s) per mole of segments. This means that the jumping

(flow) process becomes very hard at T_g in agreement with the experimental fact, ⁽⁶⁾ $\eta_S \approx 10^{13}$.

(2) Next we consider the relationship represented by equation (8).

The left-hand-side term of the latter is rewritten in the following form:

$$\frac{a'E_g}{RT_g} \frac{1}{(X_g-1)} = \frac{a'E_g}{RT_g} \frac{V_g}{V_{fg}} \frac{V_f}{V_g} \\ = 39 \frac{a'E_g}{RT_g}, \dots\dots\dots(11)$$

where the relations, $V_{fg}/V_g=1/40$ and $V_f/V_g=39/40$ were substituted. From equation (4b), the first left-hand-side term of equation (11) is understood as the reduced activation energy at T_g of the flow process. Below, the activation energy is discussed in more detail.

In deriving equation (1), it was assumed that the activation energy E^* is proportional to E_g and inversely proportional to n_h (the number of holes around a jumping segment). i. e.,

$$E^* = a'E_g/n_h = a'E_g/[(V-V_f)/V_g], \dots\dots\dots(12)$$

where a hole of molecular size was assumed, and a' is a proportionality constant. Thus, $a'E_g$ is considered as the activation energy when $n_h=1$. If there is one hole adjacent to a segment, and the latter has a thermal energy, RT_g , it will be able to jump into the hole. Thus, the activation energy $a'E_g$ will be equal to RT_g , i. e., the relation,

$$a'E_g/RT_g \approx 1, \dots\dots\dots(13)$$

is considered to be very reasonable. Introducing equation (13) into (11), one readily obtains equation (8) since $39 \approx 40$ in our approximation. Equation (13) is also a natural consequence from equation (8) if $V_{fg}/V_g \approx 1/40$. Thus, equation (13) seems to be a general relation for glass-forming liquids.

In connection with the activation energy, the following discussion will be of interest. Let ΔS_g be the entropy change associated with the glass transition. The following values of ΔS_g were reported in the literature: $\Delta S_g \approx 1.6$ to 2.3 eu/mole for polyethylene, ⁽¹⁵⁾ 1.2 eu/mole for polypropylene, ⁽¹⁷⁾ and 2.7 eu/mole for polystyrene. ⁽¹⁸⁾ The average value of ΔS_g , 2 eu/mole, is very close to the ΔS for fusion of Ar (3 eu/mole). From this fact, it may be con-

cluded that the polymer segments behave at T_g like nonpolar symmetrical molecules. Thus, the above mentioned discussion concerning equation (13) seems plausible.

(3) From equations (12) and (13), the following equation is derived:

$$E^* = RT_g \frac{V_g}{V_{fg}}, \dots\dots\dots(14)$$

The activation energy E^* at T_g is calculated from equation (14), i. e.

$$E_g^* = RT_g \frac{V_f}{V_{fg}} \frac{V_g}{V_f} = 39RT_g. \dots\dots\dots(15)$$

For polyethylene ($T_g=188^\circ\text{K}$), ⁽⁶⁾ polypropylene ($T_g=255^\circ\text{K}$), ⁽¹⁵⁾ polystyrene ($T_g=373^\circ\text{K}$), ⁽¹⁸⁾ and polyisobutylene ($T_g=203^\circ\text{K}$), ⁽¹³⁾ the values of E_g^* are 14.5 , 19.6 , 28.8 and 15.7 kcal/mole, respectively.

Previously, we noted that ΔS_g for the glass transition is about 2 eu/mole which is similar to ΔS for melting of Ar (3 eu/mole). This fact indicates that a partial Brownian motion of polymer segments starts at T_g . The motion will be not only a translational but also an internal molecular motion associated with the "trans-gauche" isomerism if the latter is possible. Since ΔS_g is 2 eu/mole, ΔE_g (energy change for the glass transition) is about $2T_g$ if the glass transition is an equilibrium phenomenon. Comparing ΔE_g with E_g^* , one immediately notices that the latter is also about 40 times as large as the former. Thus, it seems that at T_g the flow motion occurs with a great hardness.

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