

Viscosities of Supercooled Water and Other Liquids

Jun Su Bahng, Sang Joon Hahn, and Mu Shik Jhon

Korea Institute of Science and Technology, Seoul, Korea.

(Received Dec. 31, 1970)

Abstract Significant structure theory has been applied to the viscosities of supercooled liquids with success. In the supercooled region, the effect of free volume decrease is so significant that the thermal effects on the solid-like volume must be considered properly.

In addition, the two state theories proposed by Jhon and Eyring for water and Litovitz et al. for boron trioxide have been successfully applied to the structure change in the liquid state.

Considered liquids are benzene, carbon tetrachloride, *p*-xylene, water and boron trioxide.

Introduction

Significant structure theory¹ has been successfully applied to many fields including the viscosities of simple liquids and of binary mixtures. Now its applications are extended to the viscosities of supercooled liquids. In this region, the effect of free volume decrease is so significant that the thermal effects on the solid-like volume must be considered properly. Structure changes in water and boron trioxide can be explained by two state theory proposed by Jhon and Eyring¹ and Litovitz et al.²

Benzene, carbon tetrachloride, *p*-xylene, water and boron trioxide will be considered here, which cover some of van der Waals liquids, one of hydrogen bonded liquids and one of glasses.

Without the use of the hybrid equation of Litovitz et al.³ the viscosities of boron trioxide can be explained according to the significant structure theory ranging from glass transition point to 1400°C.

Theory

According to the significant liquid structure theory¹ the viscosity equation η is given as follows;

$$\eta = \frac{V_s}{V} \eta_s + \frac{V - V_s}{V} \eta_g \quad (1)$$

Here V , V_s , η_s and η_g are the molar volume of liquid, that of solid-like molecules, the viscosity of solid-like molecules and that of gas-like molecules, respectively.

The viscosity of solid-like molecules for simple liquids which show no structure change becomes,

$$\eta_s = \frac{Nh}{Z\kappa} \frac{V}{V_s} \frac{6}{\sqrt{2}} \frac{1}{1 - e^{-V/V_s}} \frac{1}{V - V_s} \exp \frac{aE_s V_s}{RT(V - V_s)} \quad (2)$$

Here a is a proportionality constant, E_s heat of molar sublimation, h the Planck constant, N

the Avogadro number, Z the number of the nearest molecules at the melting point, κ the transmission coefficient and θ the Einstein characteristic temperature.

The viscosity of gas-like molecules is,

$$\eta_g = \frac{2}{3d^2} \left(\frac{mkT}{\pi^3} \right)^{\frac{1}{2}} \quad (3)$$

Here d indicates the molecular diameter, m the mass of a molecule and k the Boltzmann constant.

Neglecting the contributions of gas-like molecules, because it is within 2% of the total,

$$\eta = \frac{Nh}{Z\kappa} \frac{6}{\sqrt{2}} \frac{1}{1-e^{-\theta/T}} \frac{1}{V-V_s} \exp\left[\frac{aE_s V_s}{RT(V-V_s)}\right] \quad (4)$$

In the supercooled region, the effect of free volume decrease is so significant that the thermal effects on the solid-like volume must be considered, i. e.,

$$V_s = V_{s0} (1 + \alpha_s(T - T_0)) \quad (5)$$

Here α_s is the thermal expansion coefficient of solid-like molecules and subscript 0 indicates the conditions of reference state (here, melting points).

For water, Jhon and Eyring assumed that there are two species of solid-like molecules, i. e., Ice-I-like molecules and Ice-III-like molecules in liquid water.

According to them, the equilibrium constant may be written as follows;

$$K = (f_{s1}/f_{s2})^q = (\exp(-\Delta H/RT) \exp(\Delta S/R) \exp(-P\Delta V/RT))^q \quad (6)$$

Here f_{s1} and f_{s2} denote the partition function for Ice-I-like and Ice-III-like molecules respectively. And q is the number of cooperatively changing molecules.

Now, the viscosity equation for water can be deduced as follows, neglecting also the contributions of gas-like molecules;

$$\eta = \frac{Nh}{Z\kappa} \frac{6}{\sqrt{2}} \frac{1}{1-e^{-\theta/T}} \frac{1}{V-V_s} \exp\left[\frac{aE_s V_s}{RT(V-V_s)}\right] (K)^{\frac{K}{(1+K)^2}} \quad (7)$$

The solid-like volume may be summed up to the mole fraction,

$$V_s = \frac{K}{1+K} V_{s1} + \frac{1}{1+K} V_{s2} \quad (8)$$

Considering thermal effects on the molar volume for Ice-I-like molecules,

$$V_{s1} = V_{s01} (1 + \alpha_1(T - T_0)) \quad (9)$$

In our calculations, α_1 and α_2 are taken as two possible values for α . For Ice-III-like molecules, the same relation applies with α_2 .

For boron trioxide, there have been many discussions^{2,4,5,6} on the viscosity-temperature relations and its structure.

Accepting the evidences of two structures in the liquid boron trioxide, the viscosity equation may be derived as water. If q molecules of structure I change cooperatively to q molecules of structure III, it can be written down as follows;

q structure I molecules \rightleftharpoons q structure III molecules. For this cooperative change, equilibrium constant K is,

$$K = (f_{s1}/f_{s2})^q = (\exp(-\Delta H/RT) \exp(\Delta S/R))$$

$$\exp(-P\Delta V/RT))^q \quad (10)$$

Now instead of Einstein oscillator, using LJD cell theory⁷ and neglecting also the contributions of gas-like molecules, the viscosity equation is rewritten as below;

$$\eta = \frac{(\pi mkT)^{\frac{1}{2}} N l_f}{2(V-V_s)\kappa} \exp\left[\frac{aE_s V_s}{(V-V_s)RT}\right] (K)^{\frac{\kappa}{(1+\kappa)^2}} \quad (11)$$

Taking logarithm, Eq. (11) becomes

$$\ln \eta (V-V_s)/T^{\frac{1}{2}} = A_0 + B_0 \frac{V_s}{(V-V_s)T} \quad (12)$$

where

$$A_0 = \ln((\pi mk)^{\frac{1}{2}} N/2\kappa) l_f \quad (13)$$

$$B_0 = aE_s/R \quad (14)$$

$$V_s = X_1 V_{s1} + X_2 V_{s2} \quad (15)$$

Considering thermal effects on solid volume, for the structure I, the following equation is given.

$$V_{s1} = V_{s01}(1 + \alpha_{s1}(T - T_0)) \quad (16)$$

For structure II, the above relation is applied with α_{s2} .

In Eq. (15), the calculated values of Litovitz et al.⁴ used for the estimations of mole fractions, which was found to be in consistency with the results of Raman spectra data. Evaluation of q is omitted because the values of $(K)^{\frac{\kappa}{(1+\kappa)^2}}$ were found to be nearly unity if q is larger than 30.

A_0 , B_0 , V_{s1} and α , have been calculated to fit the viscosity data by means of least square

method. The values of V_{s1} and α , are consistent with the observed values of boron trioxide^{2,4}

Results and Discussions

Without considering the thermal effects, benzene, carbon tetrachloride and *p*-xylene showed remarkable deviations in the supercooled region, but with the choice of reasonable α , values, good agreement between theory and experiment has been obtained.

The parametric values of a , E_s , V_s , and θ are taken from Liang et al.⁸ and Jhon et al.⁹ that of $Z\kappa$ from Bahng et al.¹⁰. The values for α , are calculated to fit the data, taken from One¹¹ and International Critical Table¹². The numerical value of α , for benzene, carbon tetrachloride and *p*-xylene is 1.9×10^{-4} , 3.3×10^{-4} and $3.6 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$, respectively. Results are shown in Fig. 1, Fig. 2, and Fig. 3.

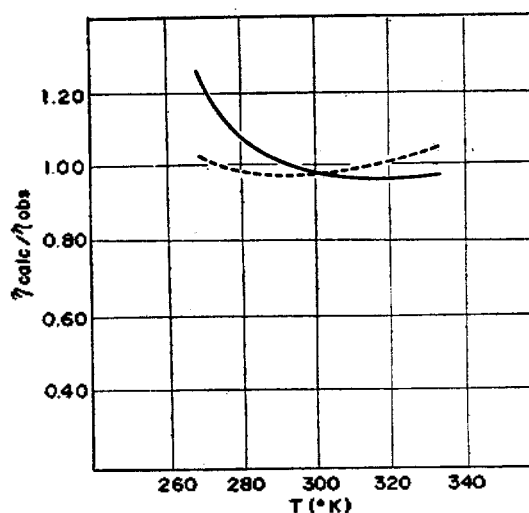


Fig. 1 Ratio of calculated values to experimental values of viscosity of benzene versus absolute temperature. Full line indicates the values calculated with $\alpha_s=0$ and the dashed line (.....) the values calculated with $\alpha_s=1.9 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$

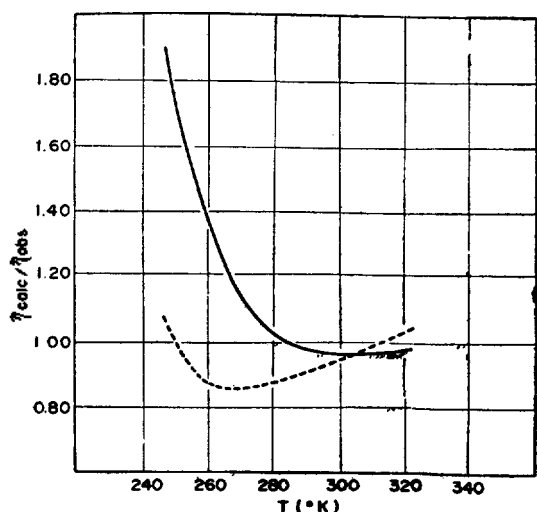


Fig. 2 Ratio of calculated values to experimental values of viscosity of carbon tetrachloride versus absolute temperature. Full line indicates the values calculated with $\alpha_1=0$ and the dashed line (.....) the values calculated with $\alpha_1=3.3 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$

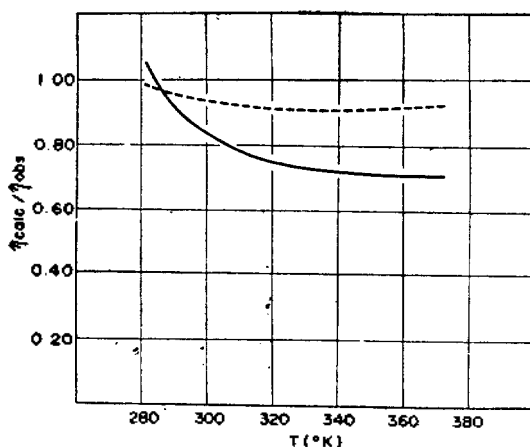


Fig. 3 Ratio of calculated values to experimental values of viscosity of *p*-xylene versus absolute temperature. Full line indicates the values calculated with $\alpha_1=0$ and the dashed line (.....) the values calculated with $\alpha_1=3.6 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$

For water, α_1 correction required is noticeably demonstrated in this case. Simple calculations without α_1 correction show negative values for

the free volume in the supercooled region. The numerical values of α_1 and α_2 for Ice-I-like molecules are "apparently" large, but it may be partly owing to the implicit inclusion of structure change effect at the melting point. The parametric values of water except α 's are taken from Jhon et al.⁹ and all α 's are calculated to fit the data, taken from Gilra¹⁴ Hallett¹⁵ and International Critical Table¹².

The numerical values for α 's are:

$$\alpha_1 = (6.41 + 0.139t) \times 10^{-3} \text{ }^\circ\text{C}^{-1}$$

$$\alpha_2 = (7.84 + 0.255t + 2.28 \times 10^{-3}t^2) \times 10^{-3} \text{ }^\circ\text{C}^{-1}$$

and

$$\alpha_3 = 1.163 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$$

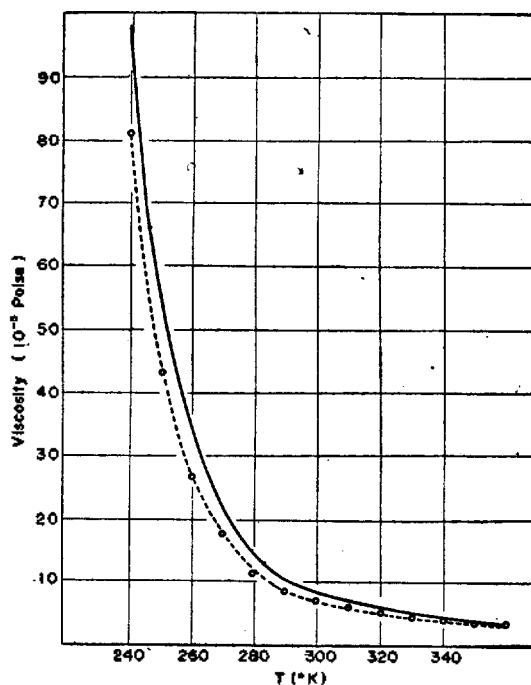


Fig. 4 Viscosity of water versus temperature. Full line indicates the values calculated with α_1 , the dashed line (.....) the values calculated with α_2 and the circles (o) experimental values.

For boron trioxide, we can get a confirmative evidence for the application of significant structure theory to calculate the viscosity, despite the extraordinary change for the values of viscosity ranging from 10 poise to 10^{13} poise. At the glass transition temperature, the calculated value is 2.77×10^{12} poise better than that of Litovitz et al.^{2,4} The numerical value of A_0 equals to -3.308 , B_0 to 1765, V_{S1} to 35.48 cm^3/mole , V_{S2} to 37.5 cm^3/mole , α_1 to $9 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ and α_2 to $9 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$.

Results are shown in Fig. 5.

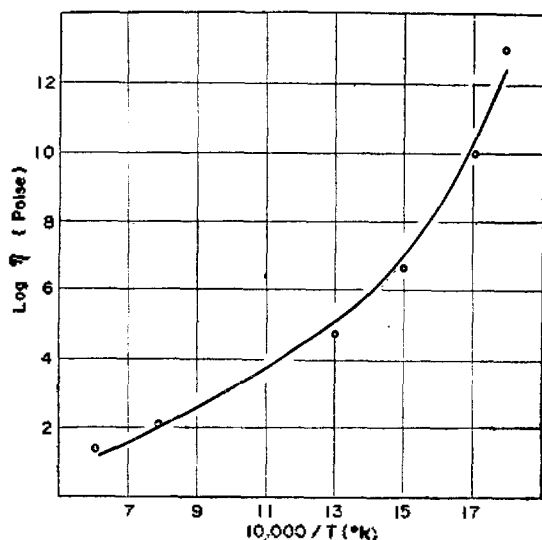


Fig. 5 Logarithm of viscosity of boron trioxide versus reciprocal absolute temperature ($10,000/T$). Full line indicates the calculated values and circles (o) the experimental values.

Bibliography

1. H. Eyring and M. S. Jhon: "Significant Liquid Structures", Jhon Wiley & Sons, Inc., N. Y. (1969).
2. P. B. Macedo, W. Capps and T. A. Litovitz; *J. Chem. Phys.*, **44**, 3357 (1966).
3. B. V. Zheleznyi; *Russ. J. Phys. Chem.*, **43**, 1311 (1969).
4. P. B. Macedo and T. A. Litovitz; *J. Chem. Phys.*, **42**, 245 (1965).
5. K. Fajans and S. W. Barber; *J. Am. Chem. Soc.*, **74**, 2761 (1952).
6. J. D. Mackenzie; *J. Am. Chem. Soc.*, **63**, 1875 (1959).
7. M. S. Jhon, W. L. Klotz and H. Eyring; *J. Chem. Phys.*, **51**, 3692 (1969).
8. K. Liang, H. Eyring and R. P. Marchi; *Proc. Natl. Acad. Sci. (U.S.)*, **52**, 1107 (1964).
9. M. S. Jhon, J. Grosh, T. Ree and H. Eyring; *Proc. Natl. Acad. Sci. (U.S.)*, **54**, 1419 (1965).
10. J. S. Bahng, S. J. Hahn and M. S. Jhon; *J. Korean Chem. Soc.*, **14**, 193 (1970).
11. T. Ono; *Low Temp. Sci., Ser. A*, **18**, 1 (1959, Japan).
12. "International Critical Table"; ed. E. W. Washburn, McGraw-Hill Book Co., Inc., N. Y. (1933).
13. M. S. Jhon, J. Grosh, T. Ree and H. Eyring; *J. Chem. Phys.*, **44**, 1465 (1966).
14. N. K. Gilra; *Canadian J. Phys.*, **46**, 2123 (1968).
15. J. Hallet; *Proc. Phys. Soc.*, **82**, 1046 (1963).