Articles

A Corresponding State Theory for the Viscosity of Liquids

Wonsoo Kim[*] and Sukbae Lee[†]

School of Materials Science and Engineering, Hongik University, Chochiwon 339-701, Korea. [*]E-mail: kws1000@freechal.com
[†]Department of Chemistry, Korea University, Seoul 136-701, Korea

A phenomenological theory of viscosity previously proposed by the present authors[8] is applied to the corresponding state theory for the viscosity of liquid. Through the process of the formulation of the corresponding state equation, we can find the simple viscosity equation with no parameters in a reduced form. The liquid viscosities of various substances can be calculated using this equation when we know only the values of the molecular weight and critical constant of substances. A corresponding state equation for the viscosity of liquid from this theory may be applicable to predicting viscosities of various substances under varying temperature and pressure. As a result, this equation may be widely applied to chemical engineering.

Key Words : Corresponding state theory, Liquid viscosity, Corresponding state equation for liquid viscosity, Theory of liquid viscosity

Introduction

Gas phase viscosity is primarily a function of momentum transfer by translation of the molecules with relatively few collisions and has been described by kinetic theory of gases. Chapman and Enskog[1] succeeded in predicting the viscosity of dilute gases by solving Boltzmann equation on the basis of bimolecular collision. This result paved the way for work to follow on the viscosity of dense gases. In liquids, however, the momentum transfer is dominated by collisions and interacting force fields between the packed molecules. The theoritical description of dense gases and liquids is difficult due to these intermolecular forces, which consists of short range effects such as repulsions and hydrogen bonding, wide range effects such as electrostatic effects and long range effects such as attraction. Statistical mechanics represents a fundamental idea about the interaction of molecules in liquid.

A theory on the viscosity of liquids was advanced by Kirkwood[2] using a statistical approach. The theory was further developed by Born and Green.[3] Since then, formal theories on the viscosity such as PNM[4] theory and BBR[5] theory have appeared. All these theories, however, fail to predict adequately the viscosity of liquids. The model theories by Andrade[6] and Eyring,[7] on the other hand, made it possible to predict the viscosity in relatively wide range of interest.

But no theory available can predict the viscosity for both gases and liquids. It is believed that the reason for the failure is a basic difference in approaching the viscosity of gases and liquids. The mechanism used for gas viscosity has been momentum transfer by intermolecular collision; the mechanism for liquid viscosity has been considered to be inter-

molecular interaction. A phenomenological theory proposed by the the present authors has been successfully applied to ideal gases and liquids,[8] van der Waals gases,[9] liquid metal,[10] and water[11,12] which exhibits abnormal behavior compared to other ordinary liquids. Besides, the viscosity at the critical point[13] and the viscosity of gas mixtures[14] could be calculated from this theory. In the present paper, a corresponding states equation for liquid viscosity is presented from this theory that had not ever been proposed. This corresponding state theory for liquid viscosity may be effectively used for the purpose of chemical engineering application

Theory of Liquid Viscosity

According to the previous theory of viscosity,[8] the viscosities of fluids through which a phonon propagates with a velocity with a velocity v and a mean free path λ can be given as follows.

$$\eta = (\sigma_k + \sigma_i)\, \lambda / v \tag{1}$$

where σ_k and σ_i are the kinetic pressure and internal pressure of the fluids respectively.

λ and v are expressed as follows;

$$\lambda = 1/(\pi d^2 N_{ph}) \tag{2}$$

$$v = (\gamma / \rho \beta)^{1/2} \tag{3}$$

where N_{ph}, ρ, β, d and γ, respectively, the phonon number density, the density of fiuids the isothermal compressibility, the collision diameter of the phonon, and the heat capacity of the ratio, C_p/C_v. If it is assumed that the number density of the phonon is proportional to molecular density and "free space" in the fluid, it can be expressed as

$$N_{ph} = (V-V_s)N/V \tag{4}$$

where V_s is the fluid volume at closed packed. N is the Avogadro's number. The quantity, $V-V_s$, corresponds to the free space. The collision diameter d can be calculated using the method of Sutherland, which is given by

$$d = d_o(1 + 1.8T_b/T)^{1/2} \tag{5}$$

where T_b is the normal boiling temperature, and d_o is the value of d at the infinite temperature. Therefore we have

$$\eta = (\sigma_k + \sigma_i)(\gamma/\rho\,\beta)^{1/2}/(\pi d^2 N_{ph}) \tag{6}$$

On the other hand, from Eq. (1) and Eq. (3) the ratio σ_k and v can be expressed as a simple form, using the following thermodynamic relationship

$$\gamma - 1 = TV\alpha^2/(C_v\beta) = MT v^2\alpha^2/C_p \tag{8}$$

where M is a molecular weight
And the result is as follows

$$\sigma_k/v = (MTC_v(1 - 1/\gamma))^{1/2}/V \tag{9}$$

By introducing Eqn. (21) into Eqn. (6), we have

$$\eta = (MTC_v(1 - 1/\gamma))^{1/2}/V(1 + \sigma_i/\sigma_k) \tag{10}$$

In a liquid state where the intermolecular forces of neighbors are so high that the internal pressure is equal to the kinetic pressure, $\sigma_i \fallingdotseq \sigma_k$, the equation of liquid viscosity is simplified as follows[15]

$$\eta = 2\lambda(MTC_v(1-1/\gamma))^{1/2}/V \tag{11}$$

Formulation of the Corresponding State Equation for the Liquid Viscosity

The vapor pressure that just suffice to liquify the fluid at critical temperature T_c is the critical pressure P_c. The molar volume occupied by the substances at T_c and P_c is the critical volume V_c. The viscosity of fluid observed at the critical point is the critical viscosity η_c. The ratio of P,V,T and η to the critical values P_c, V_c, T_c, and η_c are called the reduced pressure, the reduced volume, the reduced temperature and the reduced viscosity. These reduced variables may be written

$$P_r = P/P_c \quad V_r = V/V_c \quad T_r = T/T_c, \quad \eta_r = \eta/\eta_c \tag{12}$$

The observation that the fluid in the same state of reduced volume and reduced temperature exert approximately the same reduced viscosity is called the principle of corresponding state.

In applying Eqn. (11) to the corresponding state equation, $0.8T_c$ is used in place of $1.8T_b$ in Eqn. (5), and the values of d_o and V_s in Eqn. (4) are assumed to depend upon the van der Waals constant b which is a function of V_c as follows

$$d_o = y(b/N)^{1/3} = y(V_c/3N)^{1/3} \tag{13}$$

$$V_s = \zeta b \tag{14}$$

where y is a parametric constant and ζ may be a function of volume or temperature. If ζ is assumed a function of reduced

volume as $f_1(V_r)$, and the value of $(C_V(1 - 1/\gamma))^{1/2}$ is also assumed a function of reduced volume as $R^{1/2}f_2(V_r)$, we can reconstitute Eqn. (11) as follows, allowing easy calculation of the liquid viscosity

$$\eta = 11.05(MTR)^{1/2}V_r f_2(V_r)/((1+0.8/T_r)(V_r - f_1(V_r))V_c^{2/3}) \tag{15}$$

where R is the gas constant. In Eqn. (15) η is in μ-poise, molecular weight M in gram, T in K, and V and V_c in cm^3.

For the purpose of formulation of the corresponding state equation for liquid viscosity, we can use Bird's viscosity equation[16] at the critical point as follows.

$$\eta_c = 61.6\,(MT_c)^{1/2}/V_c^{2/3} \tag{16}$$

Therefore, we can obtain the corresponding state equation of liquid viscosity η_r as follows.

$$\eta_r = \eta/\eta_c = 0.522T_r^{1/2}V_r f_2(V_r)/((1+0.8/T_r)(V_r - f_1(V_r))) \tag{17}$$

Results and Discussion

To check that the Eqn. (11) is suitable for the calculation of liquid viscosity, we fix the parametric values of d_o and V_s as listed in Table 1. The calculated viscosities by using Eqn. (11) for argon, nitrogen, methane, carbon tetrachloride and benzene are compared with the experimental values as shown in Figures 1 through 5. As shown in those Figures, the calculated viscosities are in good agreements with those of experimental data. The viscosity equation (15), on the other hand, is consists of only reduced variables with no parameters, it may be suitable to calculate easily the liquid viscosity. To calculate the liquid viscosity from Eqn. (15), we take the values of $f_1(V_r)$ and $f_2(V_r)$ as follows.

$$f_1(V_r) = 0.3/V_r^{0.1733} + 0.02/V_r^{1.5} - 0.005/V_r^{3.35} \tag{18}$$

$$f_2(V_r) = (1/V_r^3)^{0.5} \tag{19}$$

Table 1. Parametric values used in calculation[8]

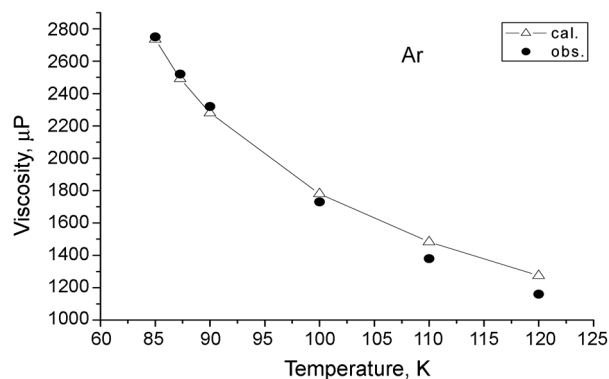|	Ar	N$_2$	CH$_4$	CCl$_4$	C$_6$H$_6$
d_o/A^o	3.418	3.749	3.882	5.881	5.349
V_s/cm^3	26.42	30.76	34.00	91.92	84.81

Figure 1. Comparison of calculated and observed values for Ar (from Eqn. (11)).

If we know the values of molecular weight and critical constants, the liquid viscosities for various substances can be obtained from the Eqn. (15). The calculated results from Eqn. (15) for above five substances are compared with the experimental values in Figures 6 through 10. Notwithstanding the use of the simple equation with no parameters, the agreements between the theoritical prediction and the experimental results are satisfactory. More accurate predictions should result when more accurate values of $f_1(V_r)$ and $f_2(V_r)$ are known.

As the experimental viscosity values at the critical point

are not known, we must use the calculated values at the critical point from Bird's equation. The calculated values at the critical point from Bird's equation are listed in Table 2. The calculated reduced viscosities for some substances from Eqn. (15) compared with those of the experimental data are shown in Figure 11, where reduced viscosity η_r is plotted at reduced temperatures, against the reduced volume. The agreements between the prediction and the experimental result are satisfactory similar to the agreements as shown in Figures 6 through 10. Although the predictions are not accurately consistent with the experimental results, this
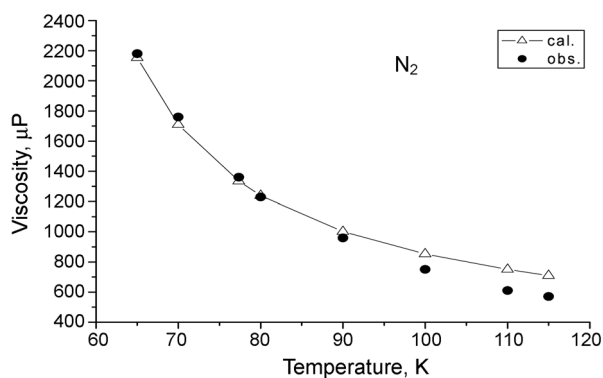

Figure 2. Comparison of calculated and observed values for N_2 (from Eqn. (11)).
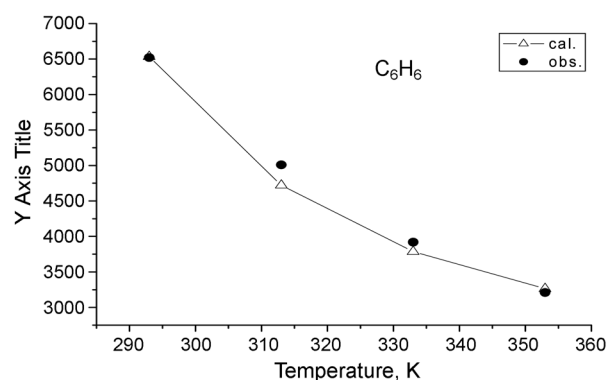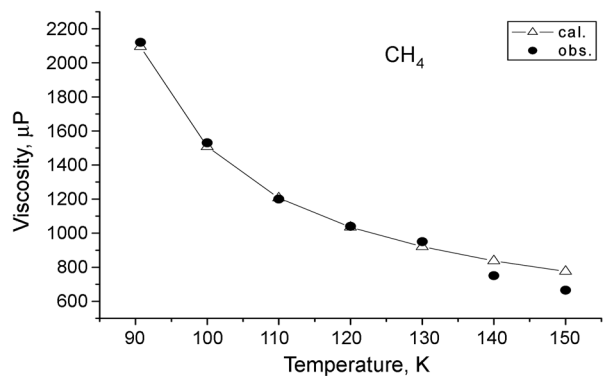

Figure 3. Comparison of calculated and observed values for CH_4 (from Eqn. (11)).
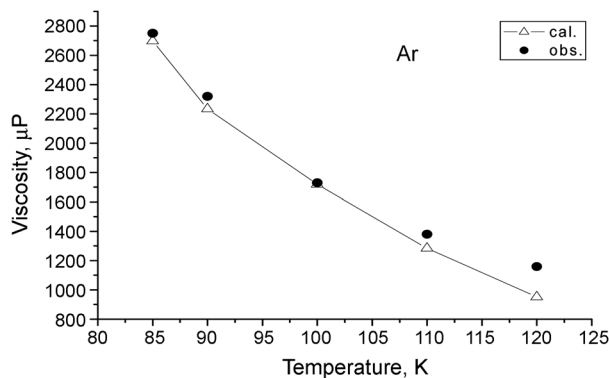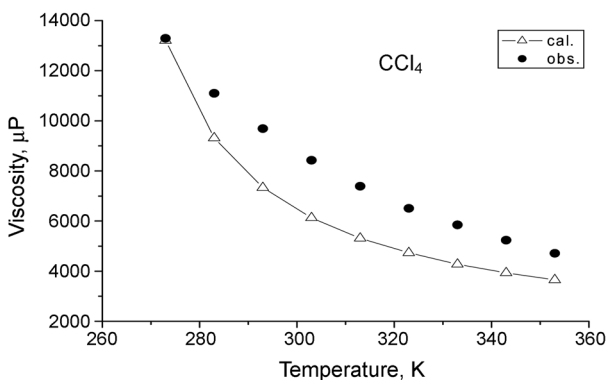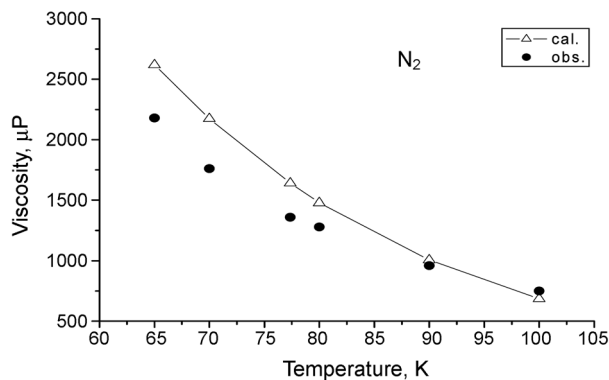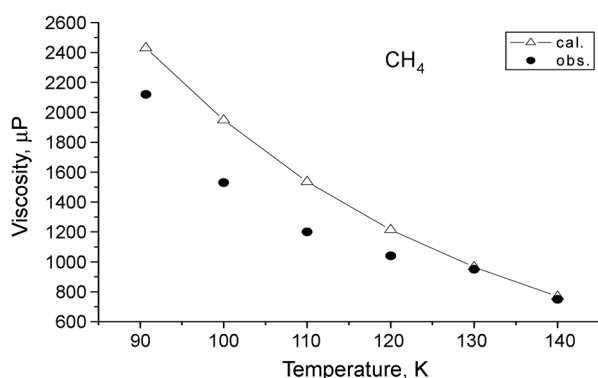

Figure 4. Comparison of calculated and observed values for CCl_4 (from Eqn. (11)).

Figure 5. Comparison of calculated and observed values for C_6H_6 (from Eqn. (11)).

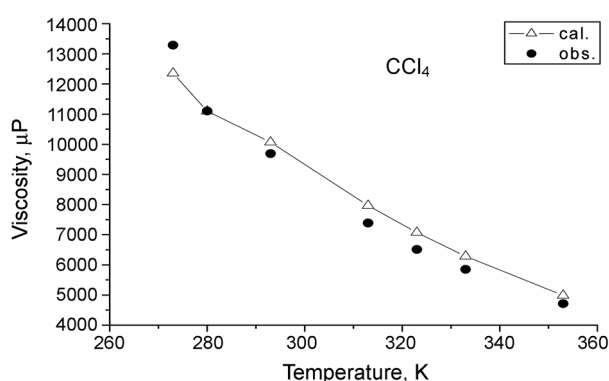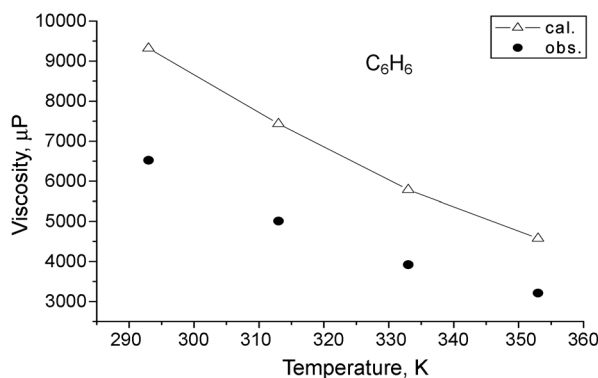**Figure 6**. Comparison of calculated and observed values for Ar (from Eqn. (11)).

Figure 7. Comparison of calculated and observed values for N_2 (from Eqn. (11)).

Figure 8. Comparison of calculated and observed values for CH_4 (from Eqn. (11)).

Figure 9. Comparison of calculated and observed values for CCl_4 (from Eqn. (11)).

Figure 10. Comparison of calculated and observed values for C_6H_6 (from Eqn. (11)).
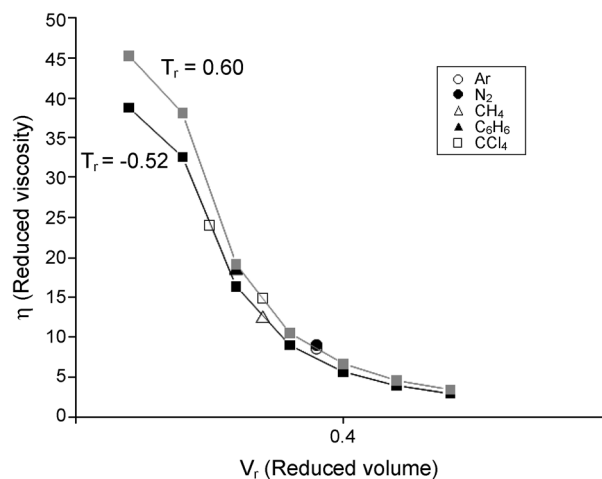
corresponding state equation may be sufficiently applied to engineering applications for the calculation of liquid viscosity because of its simplicity.

Conclusion

In spite of the practical and theoritical importance, few theories have been developed for the corresponding state equation for the fluid viscosity. Though the corresponding state theories that could be used only for gases were proposed, but they[17,18] were able to be applied at low pressures.

Table 2. The Calculated viscosity values at the critical point by Bird

Substances	Calculated Values μ-poise	Experimental Values μ-poise
Ar	269	
N_2	183	
CH_4	159	
CCl_4	425	
C_6H_6	317	

Figure 11. Reduced viscosity as a function of reduced state variables.

Through the process of the formulation of corresponding state theory for liquid viscosity, we has led to the following conclusion

(1) No theory available can predict the liquid viscosity with no parameters. But we can obtain the equation in reduced variables with no parameters, allowing easy calculation of the liquid viscosity for various substances.

(2) Using the viscosity equation at the critical point by Bird, we can propose the corresponding state of equation for liquid viscosity, and the calculated results compared with the observed values are satisfactory.

(3) If we know the values of temperature and volume under pressures, the liquid viscosities of various substances may be calculated under varying temperature and pressure. Therefore, chemical engineers can use this corresponding equation for liquid viscosity for the purpose of engineering application

References

1. Chapman, S.; Cowling, T. G. *The Mathematical Theory of Non-uniform Gases*; Cambridge University Press: 1939; chapter 16.
2. Kirkwood, J. G. *J. Chem. Phys.* **1946**, *14*, 180.
3. Born, M.; Green, H. S. *A General Kinetic Theory of Liquids*; University Press: Cambridge, 1949.
4. Prigogine, I.; Nicolis, G.; Misgusih, J. *J. Chem. Phys.* **1966**, *45*,

1086.

5. Berne, B. J.; Boon, J. P.; Rice, S. A. *J. Chem. Phys.* **1966**, *45*, 1086.
6. Andrade, E. N. *Phil. Mag.* **1934**, *S7 17*, 497.
7. Eyring, H. *J. Chem. Phys.* **1961**, *34*, 2144.
8. Kim, W.; Chair, T. S. *Bull. Korean Chem. Soc.* **1988**, *9*, 214.
9. Chair, T. S.; Kim, W.; Pak, H.; Jhon, M. S. *Korean J. of Chem. Eng.* **1989**, *6*, 121.
10. Kim, W.; Chair, T. S. *Bull. Korean Chem. Soc.* **1990**, *11*, 447.
11. Kim, W.; Chair, T. S. *Korean J. of Chem. Eng.* **1993**, *10*, 124.
12. Kim, W.; Chair, T. S. *J. Korean Chem. Soc.* **1997**, *41*, 52.
13. Kim, W.; Chair, T. S. *Bull. Korean Chem. Soc.* **2002**, *23*, 1524.
14. Kim, W. *J. Korean Chem. Soc.* **2004**, *48*, 243.
15. Kim, W.; Chair, T. S. *Bull. Korean Chem. Soc.* **2001**, *22*, 43.
16. Bird, R. B. *Transport Phenomena*; John Wiley & Sons, Inc.: 1960; p 744.
17. Poling, B. E.; Prausnitz, J. M.; O'connell, J. P. *The Properties of Gases and Liquids*, 5rd ed.; MacGraw-Hill: New York, 2001.
18. Lucas, K. *Chem. Ing. Tech.* **1981**, *53*, 959.