

NOTE

A PREDICTION OF THE ABNORMAL BEHAVIOR IN THE VISCOSITY OF LIQUID WATER UNDER PRESSURE

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Abstract—A phenomenological theory of viscosity proposed by authors was applied to liquid water under high pressure. Thermodynamic properties used in the calculation were obtained by using the theory of liquid proposed by Pak [13]. The calculated viscosities decreased abnormally with increasing pressure. We found this behavior was due to the decrease of the absolute value of kinetic and internal pressure with the pressure increase near 273.15 K.

INTRODUCTION

Liquid water exhibits a variety of unusual properties. It shows a maximum density at 4°C. Compared with other hydrogenated compound of the oxygen family, it has higher melting and boiling points, heats of fusion and vaporization, heat capacity and surface tension much higher than expected. One of the striking anomalies of water is its viscosity. The viscosity of liquid water shows a peculiar decrease with increasing pressure [1-4], which is not shown in any other liquids. The explanation of this anomaly is not clear. Some theories [5-7] had been applied to the calculation of the viscosity. But these theories retain many assumptions and adjustable parameters to fit the experimental values. In this paper we explain the anomaly with increasing pressure and reproduce the decrease by using the theory of viscosity by authors [8] which had been successfully applied to the normal liquids and gases [9], the abnormality of gases near the critical points [10], liquids under high pressure [11] and liquid metals [12].

THEORY

According to the previous theory of viscosity [8], the viscosities of fluids through which a phonon propagates with a velocity V_{ph} and a mean free path λ_{ph} can be given as follows

$$\eta = (\sigma_k + \sigma_i) \lambda_{ph} / V_{ph} \quad (1)$$

where σ_k and σ_i are the kinetic pressure and internal

pressure of the fluid respectively. Viscosity can not have the negative quantity, it should be expressed as the following form

$$\begin{aligned} \sigma_k + \sigma_i &= \left| T \left(\frac{\partial P}{\partial T} \right)_r \right| + \left| T \left(\frac{\partial P}{\partial T} \right)_r - P \right| \\ &= \left| T \alpha_p / \beta_T \right| + \left| T \alpha_p / \beta_T - P \right| \end{aligned} \quad (2)$$

V_{ph} and λ_{ph} are expressed as follows

$$V_{ph} = (\gamma / \rho \beta_T)^{1/2} \quad (3)$$

$$\lambda_{ph} = 1 / (\pi d^2 N_{ph}) \quad (4)$$

where N_{ph} is the phonon number density, ρ the liquid density, β_T the isothermal compressibility, and γ the heat capacity ratio C_p/C_v . Therefore we have

$$\eta = (|T \alpha_p / \beta_T| + |T \alpha_p / \beta_T - P|) (\rho \beta_T / \gamma)^{1/2} (\pi d^2 N_{ph})^{-1} \quad (5)$$

For the calculation of the viscosity of liquid water under high pressure, we have to know the thermodynamic properties such as α_p , β_T and γ . But unfortunately the experimental values of such properties of liquid water have not been found at high pressure. But we can estimate the viscosity at high pressure by using the state equation of the liquid. According to the Pak's theory [13], the partition function Q of the liquid is given as follows.

$$Q = \frac{N_i !}{N_i ! (N_i - N_s !)} \left[\frac{\exp(E_s / RT)}{\Pi (1 - \exp(-h\nu_i / kT))} \right]^{N_s} \left(\frac{(2\pi mkT)^{3/2} (V - V_s) \exp(E_g / RT) \pi^{1/2}}{h^3} \right)$$

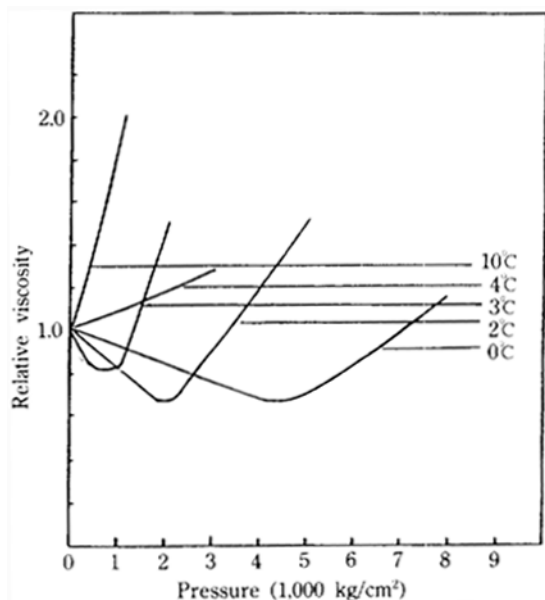


Fig. 1. Calculated relative viscosity as a function of temperature and pressure.

$$\frac{(8\pi^2 kT)^{3/2} (I_A I_B I_C)^{1/2}}{2h^3 \Pi [(1 - \exp(-h\nu_j/kT))]^{1/2}} \left(\frac{1}{N_g!} \right) \quad (6)$$

The parametric values E_s , E_g and V_s can be found by the use of following condition under the ordinary equilibrium vapor pressure

$$P = -(\partial A / \partial V)_{T,N} \quad (7)$$

$$S = -(\partial A / \partial T)_{V,N} \quad (8)$$

$$A + PV = A_g + PV_g \quad (9)$$

where A_g and V_g are the Helmholtz free energy and the volume of the vapor which is in thermal equilibrium with the liquid. By using Eqs. (7), (8) and (9) we can get the various thermodynamic properties used in the calculation of viscosity at high pressure.

RESULT AND DISCUSSION

We calculated the viscosity of liquid water by using the thermodynamic properties. In Fig. 1, we can see decrease in viscosity with increase in pressure. The experimental values were obtained by using the falling body type viscometer [3] as shown Fig. 2. The viscometer consists of a stainless steel tube containing two sinkers with high and low densities. Measurements were made by inverting the pressure vessel containing the viscometer and by recording the falling time of

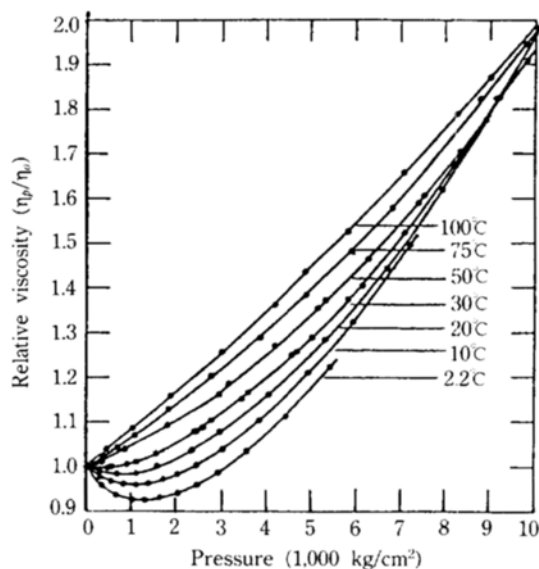


Fig. 2. Experimental values of relative viscosity of liquid water.

each sinker through the water with an electronic timer actuated by an electrical induction system. The measured viscosities go through a minimum, and then increase steadily with increasing pressure. The pressure effect on the relative viscosity is greatest at 0°C. With increasing temperature, however, the effect disappears gradually. This unusual behavior has not been proved yet. However, we may explain this phenomenon through our viscosity theory. The experimental values of σ_k and σ_l are negative between 0°C and 4°C because the α_p is negative, but the absolute values of σ_k and σ_l are greatest at 0°C and decrease with increasing pressure. In Eq. (5) the magnitude of the viscosity depends upon the absolute values of σ_k , σ_l and β_T . The β_T of water decreases with increasing temperature between 0°C and 50°C [16] at the equilibrium pressure. Therefore we can see that the decrease in viscosity with increasing pressure is due to the decrease of the absolute values of σ_k , σ_l and β_T with increasing pressure as shown in Fig. 1. Though the thermodynamic properties used in the calculation are obtained from the theoretical partition function which can not correctly predict thermodynamic properties at high pressures, the trends of the calculated viscosities as a function of pressure are similar to those of the experimental values as shown in Fig. 2. More accurate predictions should result when more accurate partition functions are known.

ACKNOWLEDGEMENT

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NOMENCLATURE

N : Avogadro number
 V : molar volume [cm^3]
 V_s : molar volume of solid-like molecule [cm^3]
 N_t : $N \times V/V_s$
 N_s : $N \times V_s/V$
 N_g : $N \times [V - V_s (= \text{free volume})/V]$
 E_s : ground state energy of solid-like molecule [J mol^{-1}]
 E_g : potential energy of gas-like molecule [J mol^{-1}]
 h : Planck constant [J sec]
 k : Boltzmann constant [J K^{-1}]
 I_a, I_b, I_c : three principal momenta of inertia [kg/m^2]
 S : entropy [e.u.]
 R : gas constant [$\text{J K}^{-1}\text{mol}^{-1}$]
 α_p : isobaric thermal expansion coefficient [K^{-1}]
 ν_i : vibrational frequency [sec^{-1}]
 β_T : isothermal compressibility [atm^{-1}]
 γ : heat capacity ratio C_p/C_v
 ρ : liquid density [g/cm^3]

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