

VISCOSITY OF AMORPHOUS SILICA WITHIN DOREMUS APPROACH

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Viscous flow of amorphous silica is described within Doremus approach assuming the forming role of defects resulting from broken silicon-oxygen bonds. It is shown that a direct consequence of defect-mediated viscous flow is the two-exponential formula of the viscosity $AT \exp(B/RT)(1 + C \exp(D/RT))$. Derived formula of viscosity has the Arrhenius-type behaviour in both high and low temperature limits and has a form similar to empirical formulae previously known for its excellent fit with experimental data. The viscosity demonstrates high activation energy at low temperatures and low activation energy at high temperatures. The activation energy of viscosity is determined by the sum of the enthalpies of formation D and motion B of defects at low temperatures $(B+D)=745$ kJ/mol and by the enthalpy of motion of defects at high temperatures $B=525$ kJ/mol. Calculated data for the viscosity of amorphous silica using the derived expression of viscosity are in excellent agreement with experimental data. Pressure dependence of viscosity is discussed.

(Key words: viscosity, network liquids, silica glass, defects, enthalpies)

1. Introduction

The viscosities of fluids are among their most important properties. Viscosity is the fundamental mechanism of dissipation of momentum in a fluid. Viscosity is described at the macroscopic level by the Navier-Stokes equations which are the equations of balance of momentum in a fluid. At the microscopic level, viscosity arises because of a transfer of momentum between fluid layers moving at different velocities as already explained by Maxwell thanks to kinetic theory. In oxide melts and glasses, viscosities determine melting conditions, temperatures of working and annealing, rate refining, maximum temperature of use, and crystallization rate. In geology magma behaviour, volcanic eruptions, and lava flow rate depend directly on silicate viscosity. Mathematically the viscosity of glasses is most exactly described by a two exponential formula [1-3]:

$$\eta(T) = AT \exp\left(\frac{B}{RT}\right) \left[1 + C \exp\left(\frac{D}{RT}\right)\right] \quad (1)$$

where T is temperature, R is molar gas constant, A , B , C and D are fitting parameters. This equation can excellently be fitted to experimental data and gives correct Arrhenius type asymptotes of viscosity at high and low temperatures. Volf gives for low and high activation energies of viscosity, e.g. coefficients B and D in equation (1): $B=80-300$ kJ/mol for low viscosity range ($\log\eta < 3$) and $(B+D)=400-800$ kJ/mol for high viscosity range ($\log\eta > 10$) [1]. A similar form equation has been derived earlier by R.W. Douglas for silicate glasses assuming that the oxygen atoms between two silicon atoms could occupy two different positions, separated by an energy barrier [3]. Equation (1) can be easily fitted within narrow temperature intervals to many approximate types of curves including known Vogel-Fulcher-Tamman and Adam-Gibbs approximations, or Kohlrausch type exponential law [4]. However in contrast to these approximations equation (1) gives correct asymptotic Arrhenius type dependences of viscosity with temperature.

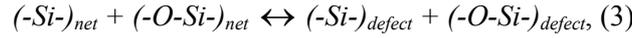
2. Net defects

Recently Doremus analysed the diffusion and viscosity in amorphous silica and shown that viscous flow is mediated by SiO molecular defects [2, 5]. Consider an ideal net representing an amorphous material, for example three-dimensional net formed via interconnecting SiO₄ tetrahedra through bridging oxygen atoms of amorphous silica. At absolute zero temperature it will contain no point

defects; however at any finite temperature T the net will contain thermally activated defects. The formation of defects in a net is determined by the creation Gibbs free energy:

$$G_d = H_d - TS_d, \quad (2)$$

where H_d is the enthalpy and S_d is the entropy of formation of net defects. Doremus suggested that diffusion of silicon and oxygen in silicate melts takes place by transport of defect SiO molecules formed in the melt. Formation of these defects creates an extra oxygen atom which leads to five-coordination of oxygen atoms around silicon moreover there is experimental evidence on five-coordination of silicon and oxygen in silicates [2, 5]. Formation of net defects can be represented by reaction:



where $(-Si-)_{net}$ and $(-O-Si-)_{net}$ belong to the net, $(-Si-)_{defect}$ and $(-O-Si-)_{defect}$ are defects created by the breaking of net. Designate the total concentration of elementary net blocks C_0 , and concentration of net defects $[(-Si-)_{defect}] = [(-O-Si-)_{defect}] = C_d$, then $[(-Si-)_{net}] = [(-O-Si-)_{net}] = (C_0 - C_d)$. Equilibrium constant of reaction (2) is determined by the change in the Gibbs free energy $G = 2G_d$:

$$K = \exp\left(-\frac{\Delta G}{RT}\right) \quad (4)$$

Equilibrium concentration of defects hence is given by equation:

$$C_d = C_0 \frac{\exp(-G_d / RT)}{1 + \exp(-G_d / RT)} \quad (5)$$

3. Viscosity within D-model

Defects mediate diffusion and viscous flow in materials. The coefficient of defect-mediated diffusion is directly proportional to the concentration of defects that mediate diffusion (C_d) and is given by equation [6]:

$$D = f\alpha_0\lambda^2\nu\left(\frac{C_d}{C_0}\right)\exp\left(\frac{S_m}{R}\right)\exp\left(-\frac{H_m}{RT}\right), \quad (6)$$

where f is the correlation factor for jumps, α_0 is determined by the symmetry, λ is jump distance, ν is a vibration frequency, S_m and H_m are the entropy and enthalpy of motion of defects. The viscosity can be found from Stokes-Einstein equation:

$$\eta(T) = \frac{kT}{6\pi rD}, \quad (7)$$

where r is the radius of defect From (7) accounting for (4) and (7) we can see that within defect-mediated model of Doremus (D-model) the viscosity is determined by equation [7, 8]:

$$\eta(T) = \frac{kT}{6\pi rD_0} \exp\left(-\frac{S_m}{R}\right) \exp\left(\frac{H_m}{RT}\right) \left[1 + \exp\left(-\frac{S_d}{R}\right) \exp\left(\frac{H_d}{RT}\right) \right], \quad (8)$$

where $D_0 = f\alpha\lambda^2\nu$. Hence parameters A , B , C and D in empirical equation (1) are as follows:

$$A = \frac{k}{6\pi rD_0} \exp\left(-\frac{S_m}{R}\right), \quad B = H_m, \quad C = \exp\left(-\frac{S_d}{R}\right), \quad D = H_d, \quad (9)$$

At high temperatures above Doremus' temperature $T \gg T_D = H_d / (R + S_d)$ the viscosity is given by a low activation energy exponential equation:

$$\eta(T) = \frac{k}{6\pi r D_0} \exp\left(-\frac{S_m}{R}\right) \left(1 + \exp\left(-\frac{S_d}{R}\right)\right) \exp\left(\frac{H_m}{RT}\right), \quad (10)$$

whereas at low temperatures $T \ll T_D = H_d / (R + S_d)$ viscosity is described by an exponential law with high activation energy:

$$\eta(T) = \frac{k}{6\pi r D_0} \exp\left(-\frac{S_m + S_d}{R}\right) \exp\left(\frac{H_m + H_d}{RT}\right), \quad (11)$$

4. Viscosity of amorphous silica

Experimental data on viscosity of amorphous silica are available from a number of experiments. Doremus recently analysed the viscosity of silica identifying among experimental data the most reliable those of [9, 10]. Fig. 1 shows the viscosity behaviour of amorphous silica comprising both experimental data from [9, 10] and the best fitted curve accordingly to equation (8). Table I gives thermodynamic parameters of net defects (presumably SiO molecules) determined by best fitted theoretical curve to experimental data.

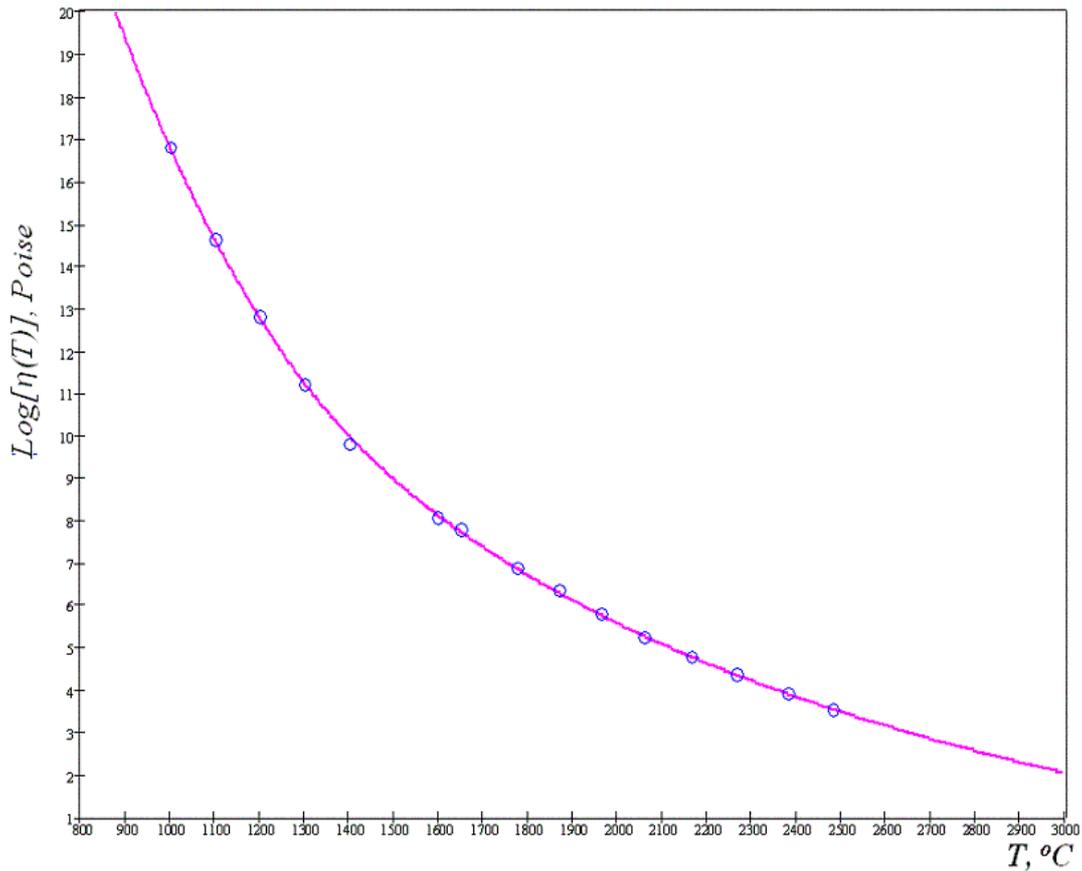


Fig. 1. Viscosity of amorphous silica. — theory, ○ experiment [8, 9].

Table 1. Thermodynamic parameters of the net defects in amorphous silica.

Parameter	H_d , kJ/mol	H_m , kJ/mol	S_d , R
Value	220	525	16.13

As seen from Fig. 1 the agreement of theory with experiment is excellent demonstrating less than 0.5% deviation of calculated from measured data. From experimental data on the viscosity of amorphous silica we obtained $H_m=525$ kJ/mol, $H_d=220$ kJ/mol which are slightly higher than those reported by Doremus: $H_m=515$ kJ/mol and $H_d=197$ kJ/mol [2, 4]. In contrast to our results Doremus' values were obtained by independent fitting of viscosity curves at high and low temperatures, e.g. using independently equations (10) and (11). We have earlier used the Doremus' values for H_d and H_m obtaining a quite satisfactory agreement with experimental data [8]. Herein we have however obtained H_m and H_d by fitting the entire viscosity curve (8) and accounting for all experimental data including those at intermediate temperatures. Thus we have obtained the most exact values of H_m and H_d from experimental data on viscosity. Current values of H_m and H_d are very close to the Doremus' data, however obtained new value of formation enthalpy $H_d=220$ kJ/mol is practically coinciding with the half of bond strength of Si in SiO_2 (443 kJ/mol [11]).

5. Pressure dependence of viscosity

Pressure dependence of viscosity is an important issue particular for planetary sciences where it determines motion of deep layers, e.g. magma under continents. Pressure dependence of viscosity can also be important for very deep disposal of nuclear waste [12-14]. A model describing pressure dependence of viscosity was suggested by Avramov in [4], where he related the viscosity to the entropy and assumed a specific pressure-dependent behaviour of volume expansion coefficient. Pressure dependence of viscosity can be derived directly from the generic formula (8) without introducing additional assumptions. Consider temperatures $T \gg T_D$ where the viscosity is given by formula (10). The pressure dependence of viscosity is given above Doremus' temperature by equation:

$$\frac{\partial \ln \eta}{\partial P} = \frac{1}{RT} \frac{\partial G_m}{\partial P}, \quad (12)$$

where defect motion Gibbs free energy is $G_m = H_m - TS_m$. The entropy of motion of defects can be related to the enthalpy of motion through Dienes ratio [15, 16]:

$$S_m = \frac{H_m}{T_f}, \quad (13)$$

where T_f is the melting temperature. The enthalpy of motion of defects is analogous to the elastic strain energy and can be estimated using the equation [8]:

$$H_m \cong \pi \mu (r - r_{dr})^2 \lambda, \quad (14)$$

where μ is the shear modulus of melt, r_{dr} is the radius of network doorway ($r > r_{dr}$). The radius of network doorway is related to ionic porosity factor $Z=1-V_i/V_m$ and can be determined through equation:

$$r_{dr} = \left(\frac{V_m - V_i}{N_A} \right)^{1/3}, \quad (15)$$

where V_m is the molar volume and V_i is the volume of ions treated as hard spheres, N_A is Avogadro's number. Resulting from (12) pressure dependence of viscosity is determined by equation:

$$\eta(P) = \eta(P_0) \exp \left[\frac{H_m(P_0)}{RT} \left(1 - \frac{T}{T_f} \right) \frac{2\kappa(P - P_0)}{3Z(\alpha - 1)} \left(1 + \frac{\kappa(2\alpha - 1)(P - P_0)}{6Z(\alpha - 1)} \right) \right] \quad (16)$$

where κ is the compressibility, e.g. $\kappa = -\frac{1}{V_m(P_0)} \frac{\partial V}{\partial P}$ and α is the ratio of defect radius to the network doorway radius, e.g. $\alpha = r/r_{dr}(P_0)$. Note that $\alpha > 1$ as $r > r_{dr}$. Equation (16) is valid at limited

pressures: $(P-P_0) \ll Z$. Note that $H_m(P_0)$ is the activation energy of viscosity at high temperatures, i.e. is a well known parameter (Table I).

Obtained equation (16) gives a similar to [4] dependence at temperatures below the melting temperature T_f . In this range the higher pressure the higher increase of viscosity. The higher compressibility and the lower ionic porosity Z the higher the deviation from a linear dependence of $\log(\eta)$ with $(P-P_0)$. Equation (16) however gives a faster decrease of pressure dependence at temperatures approaching T_f comparing with results of [4]. Moreover above the melting temperature the viscosity dependence on pressure changes the sign. At $T > T_f$ pressure causes a decrease of viscosity: in this temperature range the higher applied pressure the lower viscosity. Although near T_f this decrease is small it can be important in estimations of materials behaviour at very high temperatures and pressures, e.g. the viscosity of very deep Earth layers can be lower than expected from normal atmospheric pressure measurements.

6. Conclusions

A direct consequence of defect-mediated diffusion is the two-exponential formula of the viscosity confirming that the viscosity of silica glass obeys the Stokes-Einstein equation at all temperatures. Viscosity of amorphous silica demonstrates Arrhenius-type behaviour in both high and low temperature limits. The activation energy of viscosity at low temperatures is 745 kJ/mol whereas at high temperatures it equals 525 kJ/mol. Activation energies of viscosity are determined by the enthalpy of formation and motion of defects which for amorphous silica were found as 220 kJ/mol and 525 kJ/mol correspondingly. Calculated data for the viscosity of amorphous silica using the derived expression of viscosity are in excellent agreement with experimental data.

7. Literature

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