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Temperature Dependence of the Viscous Flow of Glass-Forming Melts in a Broad Temperature Range

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Abstract—An equation which is able to describe the temperature dependence of the viscous flow of glass-forming melts in a broad range, including the glass-transition range and elevated temperatures has been obtained. The equation contains three parameters; one of them is the preexponential multiplier, which is defined by the extension of the viscosity curve to elevated temperatures (using the Lagrange polynomial), and the other two, the delocalization energy of the atom and the transition potential of the particle, are adjustable parameters. The delocalization energy of the atom that is determined by adjustment is in sufficient accordance with the calculation according to the model of delocalized atoms. The nature of the viscous flow of glass and its melts is discussed.

Keywords: viscous flow, model, glass and its melts, delocalization of an atom, structural change, bridge atom

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INTRODUCTION

The most popular expression for the description of the temperature dependence of the viscosity of liquids $\eta(T)$ is the Eyring equation [1]:

$$\eta = \eta_0 \exp\left[\frac{\Delta F_\eta(T)}{RT}\right], \tag{1}$$

where $\Delta F_\eta(T)$ is the free activation energy of viscous flow, R is a gas constant, η_0 is the preexponential multiplier $\eta_0 = h/v_\eta$, h is Planck's constant, and v_η is the volume of the kinetic unit which is responsible for fluidity.

Nemilov et al [2–5] suggested the valence-configurational theory of the viscous flow, according to which the free activation energy comprises the sum of the switching potential of the bridging valence bond ΔF_η^0 and the potential of the configurational change of structure around bond switching $\Delta F_{\eta k}(T)$:

$$\Delta F_\eta(T) = \Delta F_\eta^0 + \Delta F_{\eta k}(T).$$

The value $\Delta F_{\eta k}(T)$ is determined from the experimental data on the configurational component of the molar heat capacity $C_{p\,\mathrm{conf}}(T)$. Good agreement between the theory and experiment was obtained. Thus, according to this theory, the temperature dependence of the viscous flow of glass-forming melts is determined by the dependence of the configurational change of the structure on temperature [2–5]. However, the explicit form of the function $\Delta F_{\eta k}(T)$ is not revealed.

Recently, a possible approach to the dependence $\eta(T)$ in the broad temperature range has been considered [6–9].

In this work, more precise derivation of the viscosity equation is suggested [8, 9], which contains three adjustable parameters rather than four as before [6–9]. It was shown that the obtained equation is in sufficient accordance with the experimental data.

THEORETICAL PART

Assume that the probability of the transition of a kinetic unit W from one equilibrium position to another is determined first by the probability of the local change of the structure W_1 at the given kinetic unit and, second, by the probability W_2 that it has sufficient energy ΔF_∞ for the transition to the new position [10, 11]

$$W = W_1 W_2. \tag{2}$$

At elevated temperatures, the molecular mobility is determined by the probability of the transition of the kinetic unit into one of the "prepared disordered microranges" of the structure, which are usually present at high temperatures ($W_1 = 1$),

$$W_2 = \exp\left(-\frac{\Delta F_\infty}{kT}\right). \tag{3}$$

In the glass transition range, the structure of the melt becomes denser with a decrease in temperature and the probability of the local change of the structure W_1 plays a significant role in the mobility of the molecules. Let us consider this concept within a two-level model of delocalized atoms [12, 13].

One of the main parameters of this model is the elementary fluctuation volume Δv_e required for the shift of the kinetic unit from equilibrium position, that is, its delocalization:

$$\Delta v_e = \frac{RT_g}{f_g B},$$

where R is the gas constant, B is the instantaneous elasticity modulus at bulk compression, and $f_g = (\Delta V_e/V)_{T=T_g}$ is the fraction of the fluctuation volume of the system that is frozen at the glass-transition temperature T_g. The fluctuation volume of the amorphous substance ΔV_e is determined by the delocalization of atoms (N_e is the number of delocalized atoms):

$$\Delta V_e = N_e \Delta v_e. \tag{4}$$

For amorphous substances of one class, $f_g \approx \text{const}$ and $(T_g/B) \approx \text{const}$; therefore, Δv_e is almost a constant value. For example, we have $\Delta v_e \approx (8\text{–}10)$ Å^3 for alkali-silicate glass [12–14]. The delocalization energy of atom for them is also low:

$$\Delta\varepsilon_e = RT_g \ln(1/f_g) \approx 20 \text{ kJ/mol}. \tag{5}$$

This value coincides with the activation energy of some relaxation processes (internal friction, dielectric losses, and others), which are related to the low-activation deformation in the silicon-oxygen network. The latter is related to the particular local shift of the bridging oxygen atom in the bridge Si–O–Si [13].

It is considered that the "atom delocalization" in inorganic glass and their melts corresponds to a slight critical shift of the bridging atom (oxygen atom in the bridge Si–O–Si), which is related to a local low-activation deformation of the valence bond network that is responsible for the formation of the delocalization volume of atom Δv_e.

The probability of the delocalization of an atom is reduced to the probability of the formation of the elementary fluctuation volume around it, which corresponds to or exceeds Δv_e.

Consider that the shift of the active bridge atom from equilibrium is accompanied by the translations of the neighboring particles and reflects the local change of the structure in amorphous substances. Assuming this, we refer to the probability of the local structural change W_1 as the probability of the delocalization of atom, which can be expressed by the following equation:

$$W_1 = \exp\left(-\frac{N}{N_e}\right), \tag{6}$$

where N is the number of atoms (kinetic units). The rationalization of the given equation is given in the Appendix.

Using the quasi-lattice model [15], let us reveal the explicit form of the temperature dependence of the number of delocalized atoms $N_e(T)$. We suggest that there are the main and excited junctions in the lattice of an amorphous medium. As one of the variants of atom excitation, assume its delocalization, at which the corresponding junction is translated from the main position as the result of the local deformation of the lattice (bond network). Let us refer to this defect translated junction of the lattice as the excited junction. Their amount corresponds to the number of delocalized atoms (N_e). The total number of junctions in the lattice, both main (N) and excited (N_e), corresponds to $(N + N_e)$.

Assuming this, we can write the following relationship for the constituent of the free energy of the system that is related to the presence of lattice defects [15]:

$$\Delta F = N_e \Delta\varepsilon_e - kT \ln\frac{(N + N_e)!}{N!\,N_e!},$$

where the expression under the logarithm represents the number of ways of the arrangement of delocalized atoms by the possible junctions and $\Delta\varepsilon_e$ is the delocalization energy of the atom.

We can show that the minimum ΔF corresponds to the following number of delocalized atoms:

$$\frac{N_e}{N} = \left[\exp\left(\frac{\Delta\varepsilon_e}{kT}\right) - 1\right]^{-1}. \tag{7}$$

Introducing this dependence $N_e(T)$ to the exponent of Eq. (6), we derive the equation for the probability of the local change of the structure $W_1(T)$ as a "double exponent":

$$W_1 = \exp\left\{-\left[\exp\left(\frac{\Delta\varepsilon_e}{kT}\right) - 1\right]\right\}. \tag{8}$$

Further, using Eqs. (3) and (8), as well as the known relationship between viscosity η and the value W in accordance with the Stokes–Einstein theory (see, for example, [16, 17])

$$\eta \sim \frac{1}{W} = \frac{1}{W_1 W_2},$$

we finally get the viscosity equation

$$\eta = \eta_0 \exp\left\{\frac{\Delta F_\infty}{kT} + \left[\exp\left(\frac{\Delta\varepsilon_e}{kT}\right) - 1\right]\right\}, \tag{9}$$

where η_0 is the proportionality coefficient (viscosity η at $T \to \infty$).

COMPARISON WITH EXPERIMENT

Three parameters are included in Eq. (9), namely, η_0, ΔF_∞, and $\Delta\varepsilon_e$. The preexponential multiplier η_0, which corresponds to the viscosity at elevated temperatures, is determined by the extension of the viscosity curve $\log\eta - 1/T$ to the temperature $T \to \infty$ (using the Lagrange polynomial) [18]. Knowing the value η_0 and adjusting the parameters ΔF_∞ and $\Delta\varepsilon_e$ by Eq. (9), we calculated the viscosity η.

We chose two-component silicate, germanate, and borate glass as the objects of study. In plots with the coordinates $\log\eta - 1/T$, the points correspond to the experimental data, whereas the curves in bold correspond to the calculation by Eq. (9). We can see that the theoretical curve fits the experimental points (Figs. 1, 2). In the table, the values of the parameters η_0, ΔF_∞, and $\Delta\varepsilon_e$ at which the calculation agrees with the experiment are given. The required experimental data on the temperature dependence of the viscosity of glass-forming melts $\eta(T)$ were taken from the SciGlass database [19].

Thus, the viscosity equation (9), which is derived from the adjusted model [8, 9], agrees well with the experimental data for glass-forming melts.

RESULTS AND DISCUSSION

It follows from the comparison of Eq. (9) with the Eyring equation (1) that the free activation energy of viscous flow $\Delta F_\eta(T)$ comprises two components:

$$\Delta F_\eta = \Delta F_\infty + RT\left[\exp\left(\frac{\Delta\varepsilon_e}{RT}\right) - 1\right], \tag{10}$$

$$\Delta F_\eta = \Delta F_\infty + \Delta F_s(T), \tag{11}$$

where ΔF_∞ is referred to as the transition potential of an atom (kinetic unit) and the second component $\Delta F_s(T)$ is the potential of the local change of structure, which is the temperature function:

$$\Delta F_s(T) = RT\left[\exp\left(\frac{\Delta\varepsilon_e}{RT}\right) - 1\right]. \tag{12}$$

One can demonstrate that Eq. (10) describes effectively the temperature dependence of the free activation energy of the viscous flow of various glass-forming melts in a broad temperature range using two adjustable parameters. This equation was obtained in the approximation of the coincidence of the preexponential multipliers in viscosity Eqs. (1) and (9).

The transition potential of the particle ΔF_∞ represents a high-temperature limit of the free activation energy of the fluidity $\Delta F_\infty = \Delta F_\eta$ ($T \to \infty$). The values $\Delta F_\infty \approx$ (90–120) kJ/mol that were obtained by adjustment (table) for alkali-silicate glass are in accordance with the limiting values of the free activation energy of the viscous flow of silicate glass at elevated temperatures (up to $T = 1573$ K) [20]: $\Delta F_\infty \approx$ 100–140 kJ/mol.

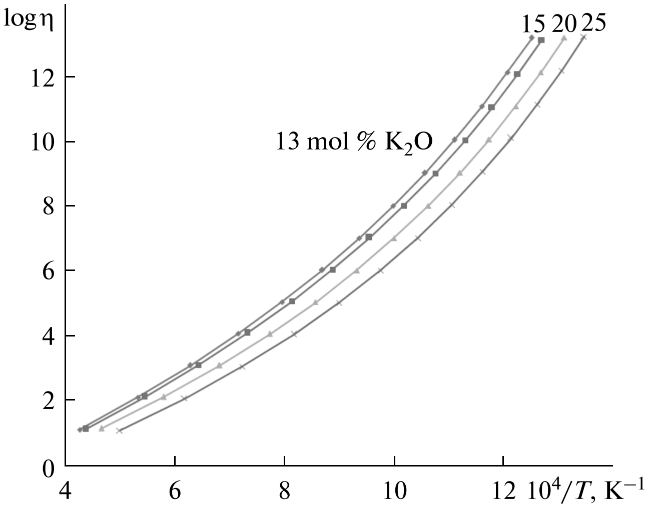

Fig. 1. Temperature dependence of the viscosity of potassium-silicate glass. The points are the experimental data and the curves represent the calculation by Eq. (9).

At $kT \gg \Delta\varepsilon_e$, Eq. (9) is transformed into usual Arrhenius exponent with constant activation energy

$$\eta = \eta_0 \exp\left(\frac{\Delta F_\infty}{kT}\right) \tag{13}$$

in accordance with the experimental data [20].

In our approach, the local change of the structure of an amorphous substance with the change of the temperature is reduced to the delocalization of the active atom. In the physical sense, in our opinion, there is in fact the local configurational change of the structure, because the critical displacement of the atom from the equilibrium position is related to the change of the configuration of the neighboring atoms. If this is the case, our results are in accordance with the representation [2–5] that the temperature dependence of viscosity in the glass-transition range is responsible for the configurational change of the structure.

The explicit form of the temperature dependence of the potential of the local change of the structure (12), which depends on the value $\Delta\varepsilon_e$, is derived from the model. The delocalization energy of atom $\Delta\varepsilon_e$ is calculated by Eq. (5) according to the model from [12]. Knowing $\Delta\varepsilon_e$, one can evaluate $\Delta F_s(T)$ by Eq. (12). For silicate glass, the calculated values $\Delta\varepsilon_e \approx$ (20–24) kJ/mol are in sufficient accordance with the data obtained by the adjustment $\Delta\varepsilon_e \approx$ (21–23) kJ/mol (table).

Although the value $\Delta\varepsilon_e$ is small, for example, $\Delta\varepsilon_e =$ 20 kJ/mol for sodium-silicate glass (26.1 mol % Na$_2$O), its introduction in the exponential depen-

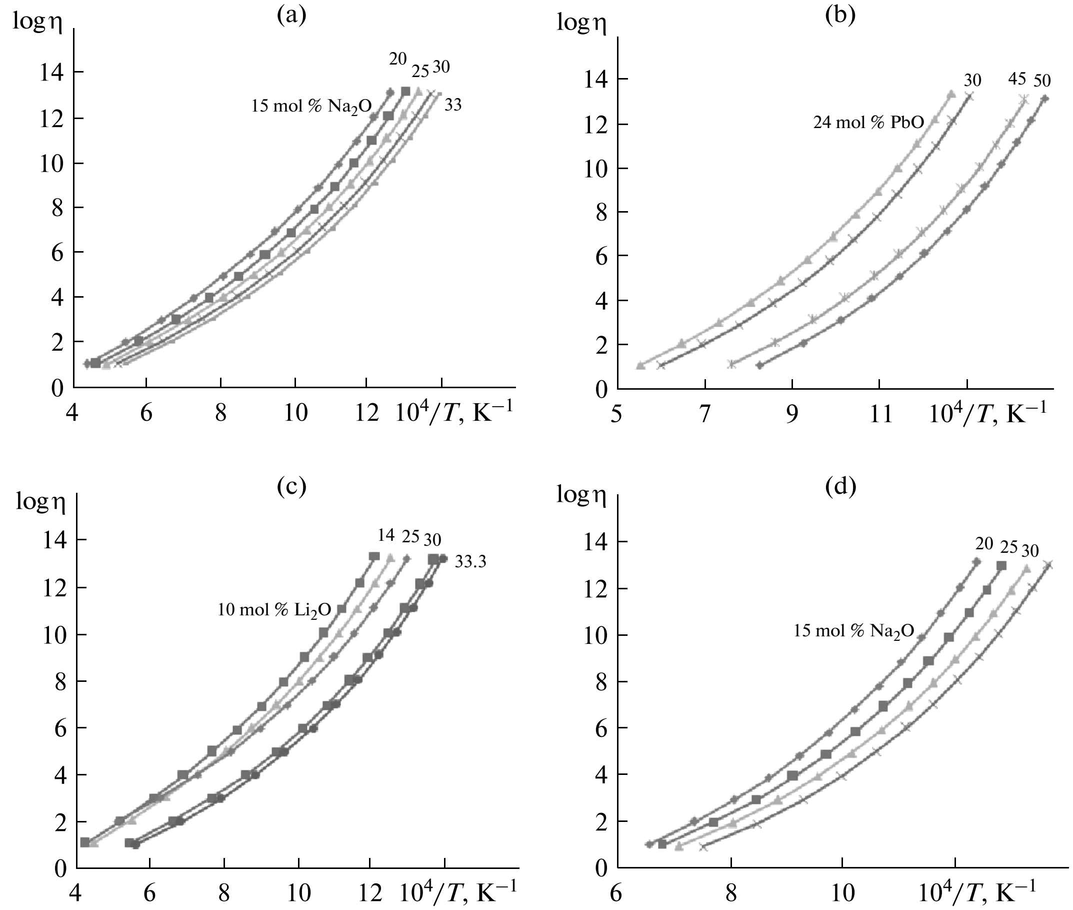

Fig. 2. Temperature dependence of the viscosity of (a) sodium-silicate, (b) lead-silicate, (c) lithium-silicate, and (d) sodium-germanate glass. The points are the experimental data and the curves represent the calculation by Eq. (9).

dence (12) at $T = T_g = 721$ K leads to a fairly high value of the potential of the local change of structure at $T = T_g$

$$\Delta F_s(T_g) = RT_g\left[\exp\left(\frac{\Delta\varepsilon_e}{RT_g}\right) - 1\right] \approx 114\ \text{kJ/mol}.$$

It corresponds to nearly half of the free activation energy of the viscous flow $\Delta F_\eta(T_g)$, as follows from the Eyring equation (1):

$$\Delta F_\eta(T_g) = RT_g \ln\left[\frac{\eta(T_g)}{\eta_0}\right] \approx 214\ \text{kJ/mol}.$$

Here, the following data are used: $T_g = 721$ K, $\eta(T_g) \approx 10^{12}$ Pa s, and $\eta_0 \approx 10^{-2.5}$ Pa s. The transition potential of atom ΔF_∞ for this glass is nearly 100 kJ/mol according to Eq. (11).

CONCLUSIONS

The consideration that the probability of the local structural change at the viscous flow of a glass-forming melt is described as the probability of the delocalization of the bound atom has been developed. The "delocalization of an atom" in inorganic glass and its melts implies the displacement of the bridging atom (of the oxygen atom type in the Si–O–Si bridge), which is related to the local low-activation viscoelastic deformation of the valence bond network. The explicit form of the temperature dependence has been suggested for the potential of the local structural change. We showed that the obtained viscosity equation is in sufficient accordance with the experimental data. In contrast with the previous variants, it contains three rather than four adjustable parameters having a particular interpretation.

APPENDIX

The variant of the rationalization of Eq. (6). Earlier, for the probability of the delocalization of an atom, the following equation was suggested [12]:

$$W_1 = \exp\left(-\frac{\Delta v_e}{v_f}\right), \tag{14}$$

Characteristics of the viscous flow of inorganic glass of the R_2O–SiO_2 (R = Li, Na, K), PbO–SiO_2, Na_2O–GeO_2, and Na_2O–B_2O_3 systems (according to the data [19])

Content of R_2O, PbO, mol %	$-\log\eta_0$ [П]	$\Delta\varepsilon_e$, kJ/mol	ΔF_∞, kJ/mol	T_g, K	$\Delta F_\eta(T_g)$, kJ/mol	f_g	$\Delta\varepsilon_e$, kJ/mol (5)
Li_2O	Li_2O–SiO_2						
10	2.55	20	127	814	245	0.028	24
14	2.57	20	120	788	237	0.028	23
25	2.41	19	91	738	219	0.028	22
30	2.25	19	78	721	212	0.028	21
33.3	2.23	19	71	708	208	0.028	21
Na_2O	Na_2O–SiO_2						
15	2.53	19	118	783	235	0.028	23
20	2.35	19	101	759	225	0.028	23
25	2.36	19	94	739	219	0.028	22
30	2.36	19	87	721	214	0.028	21
33	2.26	19	78	712	209	0.028	21
K_2O	K_2O–SiO_2						
13	2.33	19	121	795	235	0.028	24
15	2.31	19	117	793	232	0.028	24
20	2.14	19	100	759	222	0.025	23
25	2.22	19	90	739	217	0.025	23
PbO	PbO–SiO_2						
25	3.15	21	100	785	245	0.027	24
30	2.95	21	79	761	234	0.027	23
45	3.34	20	57	696	218	0.027	21
50	3.33	19	42	674	212	0.027	20
Na_2O	Na_2O–Ge_2O						
15	3.81	22	79	801	259	0.026	24
20	3.21	22	58	773	241	0.027	23
25	3.10	21	49	749	232	0.027	22
30	3.12	21	40	727	225	0.027	22
Na_2O	Na_2O–B_2O_3						
10	3.45	18	47	618	194	0.026	19
15	3.93	20	44	680	221	0.026	21
20	3.41	21	26	727	229	0.026	22
25	3.77	22	19	735	237	0.026	22
30	4.45	23	3	748	250	0.025	23

where v_f is the mean fluctuation volume on a kinetic unit,

$$v_f = \frac{\Delta V_e}{N}. \quad (15)$$

In accordance with Eq. (4), the elementary fluctuation volume Δv_e, which is required for the delocalization of an active atom, is

$$\Delta v_e = \frac{\Delta V_e}{N_e}. \quad (16)$$

From here, introducing Eqs. (15) and (16) in exponent (14), we obtain Eq. (6):

$$W_1 = \exp\left(-\frac{N}{N_e}\right).$$

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