



## Equations of viscous flow of silicate liquids with different approaches for universality of high temperature viscosity limit

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### Abstract

The Vogel-Fulcher-Tammann (VFT), Avramov and Milchev (AM) as well as Mauro, Yue, Ellison, Gupta and Allan (MYEGA) functions of viscous flow are analysed when the compositionally independent high temperature viscosity limit is introduced instead of the compositionally dependent parameter  $\eta_{\infty}$ . Two different approaches are adopted. In the first approach, it is assumed that each model should have its own (average) high-temperature viscosity parameter  $\eta_{\infty}$ . In that case,  $\eta_{\infty}$  is different for each of these three models. In the second approach, it is assumed that the high-temperature viscosity is a truly universal value, independent of the model. In this case, the parameter  $\eta_{\infty}$  would be the same and would have the same value:  $\log \eta_{\infty} = -1.93 \text{ dPa}\cdot\text{s}$  for all three models. 3D diagrams can successfully predict the difference in behaviour of viscous functions when average or universal high temperature limit is applied in calculations. The values of the AM functions depend, to a greater extent, on whether the average or the universal value for  $\eta_{\infty}$  is used which is not the case with the VFT model. Our tests and values of standard error of estimate (SEE) show that there are no general rules whether the average or universal high temperature viscosity limit should be applied to get the best agreement with the experimental functions.

**Keywords:** glasses, silicate, thermal properties, viscosity, modelling

### I. Introduction

Viscosity determines whether materials behave fluid-like or have properties of rigid bodies. Viscosity of glass-forming melts increases sharply when temperature  $T$  decreases. There are a plethora of studies analysing the temperature dependence of viscosity.

The most popular viscosity model with three parameters is the Vogel-Fulcher-Tammann (VFT) equation [1–3]:

$$\log \eta_{VFT}(T, x) = \log \eta_{\infty V} + \frac{B(x)}{T - T_o(x)} \quad (1)$$

where  $T$  is temperature and  $x$  is composition i.e. “molar fraction”. The constant  $B(x)$  and the pre-exponential factor  $\eta_{\infty V}$ , as well as a finite temperature  $T_o(x)$  at which the viscous flow ceases, are three parameters that can be determined by fitting.

Avramov and Milchev proposed [4–7] an alternative

model (AM model) which is based on the temperature dependence of average jump frequency. In this model, the number of free parameters of the viscosity equation is reduced by assuming that at the referential temperature  $T_r$  the viscosity is  $10^{13} \text{ dPa}\cdot\text{s}$  [8]. Therefore, the AM equation has the form:

$$\log \eta_{AM}(T, x) = \log \eta_{\infty A} + (13 - \log \eta_{\infty A}) \left( \frac{T_r}{T} \right)^{\alpha} \quad (2)$$

where fitting parameters are the pre-exponential factor  $\eta_{\infty A}$ , the “fragility” parameter  $\alpha$  and the referential temperature  $T_r$ . Parameter  $\alpha$  can be related to the kinetic fragility parameter  $m$  by following expression  $\alpha = m/(13 \log \eta_{\infty A})$  [8,9]. According to Angel [10,11], the fragility parameter  $m$  is the slope of the viscosity curve near glass transition temperature  $T_g$ , that is  $m = d(\log \eta)/d(T_g/T)|_{T=T_g}$ .

Recently, Mauro, Yue, Ellison, Gupta and Allan [12] presented a new model for the viscosity of glass forming liquids (MYEGA model). This model starts from the Adam-Gibbs equation [13], relating viscosity to

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the configurational entropy and the temperature dependent constraint model of Gupta and Mauro [14]. When  $\log \eta_{rr} = 13$  dPa·s, the MYEGA equation [12] for viscous flow is transformed into the following equation:

$$\log \eta_{MYEGA}(T, x) = \log \eta_{\infty M} + (3) \\ + (13 - \log \eta_{\infty M}) \frac{T_r}{T} \exp \left[ \left( \frac{m}{13 - \log \eta_{\infty M}} - 1 \right) \left( \frac{T_r}{T} - 1 \right) \right]$$

The extrapolated infinite temperature viscosity in Eq. 3 is denoted as  $\log \eta_{\infty M}$ .

There are several important studies concerning pre-exponential parameter  $\eta_{\infty}$  of viscosity equation. Nemilov [15] derived the following equation  $F_{\infty} = \Delta G^*/V_{\eta}$  that relates to free energy of activation of viscous flow  $\Delta G^*$ , the instantaneous shear modulus  $F_{\infty}$  and the volume  $V_{\eta}$  of kinetic units that overcame activation barrier. In his analyses, the relationship  $\eta = (N_A \cdot h/V_{\eta}) \cdot \exp(\Delta G^*/RT)$  for viscosity has been used, where  $N_A$  is Avogadro's number,  $h$  is Planck's constant and  $R$  is universal gas constant. He gave the proof that independently of the chosen molecular model the pre-exponential parameter  $\eta_{\infty}$  in different viscosity equations is determined by the molecular or atomic volume of the particle  $V_{\eta}$  responsible for viscous flow, and that the most common expression for  $\eta_{\infty}$  is Eyring's  $\eta_{\infty} = N_A \cdot h/V_{\eta}$  [15,16].

For the diversity of oxide systems (silicate, borate, metaphosphate, germanate, lanthanum oxide glass etc.), the value of  $V_{\eta}$  is in the range of 9–14 cm<sup>3</sup>/mole and generally correlates with the volume of bridge oxygen ion in the bridge of the –Si–O–Si– type.

Values of  $V_{\eta}$  for chalcogenide glasses are approximately twice as bigger and correspond to the volume of chalcogen in the bridges like –As–S–As–, –As–Se–As– etc. As a result, Nemilov [15,16] concludes that in inorganic glasses, the value of  $\eta_{\infty}$  is determined by the volume of bridge atoms in the bridges like –Si–O–Si– and –As–Se–As–. For oxide melts and glasses it holds that  $\eta_{\infty} \approx \text{const} \approx 10^{-2.5}$  Pa·s.

Sanditov *et al.* [17] started from the viscosity equation  $\eta = \eta_{\infty} \cdot \exp(E_{\eta}/RT)$ , where  $E_{\eta}$  is the free energy of activation of viscous flow and  $\eta_{\infty}$  pre-exponential factor. The following relationships between the free activation energy, the heat  $H_{\eta}$  and the activation entropy of viscous flow  $S_{\eta}$  is fulfilled:  $E_{\eta} = H_{\eta} - T \cdot S_{\eta}$ . Taking this into account, the viscosity equation could be rewritten as  $\eta = \eta_{\infty} \cdot \exp(H_{\eta}/RT)$ , where the experimental value of pre-exponential factor  $\eta_{\infty}$  includes entropy  $\eta_{\infty} = \eta_{\infty} \cdot \exp(-S_{\eta}/RT)$ . The expression for  $\eta_{\infty}$  is Eyring's  $\eta_{\infty} = N_A \cdot h/V_{\eta}$ . The entropy of activation is equal to zero when ( $T \rightarrow \infty$ ) and factor  $\eta_{\infty}$  is equal to viscosity of substance in gaseous state. Sanditov *et al.* [17] have calculated the pre-exponential factor for germanate and borate glass forming liquids with the use of Lagrange interpolation formula. The pre-exponential factor weakly depends on the nature of glass. Recently, Sanditov has

proposed a model of viscous flow of glass forming liquids and glasses [18]. According to this model, local low-activation deformation of the network of covalent bonds is necessary condition for viscous flow. The displacement of a bridging oxygen atom leads to the switch of bond in silicate glasses. The pre-exponential factor  $\eta_{\infty}$  in the obtained equation for viscosity as a function of temperature is  $\eta_{\infty} = h/V_{\eta}$ , where  $V_{\eta}$  is the volume of a particle surmounting a potential barrier.

The question is, whether parameters  $\eta_{\infty}$  in Eqs. 1–3 are dependent on composition and should they have the same values or not. The comparison with the other two models has shown that the distribution of  $\eta_{\infty M}$  values is the narrowest with MYEGA [12], which is in agreement with the concept of universality of the  $\eta_{\infty}$  parameter for the given class of materials [19–21]. With the assumption of the universal high temperature limit of viscosity, Angel [22] proposed that non-Arrhenius plot is directly connected to  $m$ . Hecksher *et al.* [23] assumed that parameters  $\eta_{\infty}$  are equal for the VFT and the AM equations. The authors fitted experimental data for 42 organic liquids and found that on average the VFT functions fit better than the AM functions. Senkov *et al.* [24] analysed the fragility behaviour of glass forming liquids, assuming that the fragility index  $m$  is unique for each material and does not depend on the model and type of the fitting function. They state that parameters  $\eta_{\infty}$  for the VFT and AM models are different and that these values depend on the type of liquid and can vary a great deal. The existence of compositional dependence of parameter  $\eta_{\infty}$  that appears in the AM function was determined by Avramov [8] on the basis of experimental data for silicates. Kozmidis-Petrovic analysed [25] the VFT, AM and MYEGA functions, using the foregoing approach of compositional dependence for parameter  $\eta_{\infty}$ . All equations for viscous flow are then expressed using the parameters characteristic for the AM model and compared directly. In doing so, it has been considered that parameters  $\eta_{\infty}$  are different for diverse models as stated by Avramov [9].

Zhang *et al.* [26] investigated the high temperature viscosity limit by analysing viscosity curves for 946 silicate liquids and 31 other liquids. They state that there is no significant dependence of the high-temperature viscosity limit on the composition  $x$ . The value for the high-temperature viscosity limit was given based on the MYEGA model. The average values that follow from the VFT and AM models are also presented there.

The direct measurement of the high-temperature viscosity limit  $\eta_{\infty}$  is not possible. The value of  $\eta_{\infty}$  could be obtained by extrapolation of measured data of viscosity or by some model particularly proposed for  $\eta_{\infty}$ . Unfortunately, the existing models such as theories proposed by Frenkel and Eyring [26] do not take into account the fragility as important characteristic of viscosity of glass-forming liquids. The theories developed for the AM and MYEGA functions from the very beginning ignored the theoretical analysis of  $\eta_{\infty}$ . But these models

include fragility and together with VFT, give three most popular equations for viscosity of glass-forming liquids. For this reason, the knowledge of the value that should be taken as  $\eta_{\infty}$  is of great practical importance.

In this paper, we will analyse the relation between the MYEGA, AM and VFT equations expressing them in such a way that their values of the high-temperature viscosity limit does not depend on chemical composition. Here, two different approaches can be adopted:

1. It can be assumed that each model should have its own high-temperature viscosity limit based on average value of  $\eta_{\infty}$  obtained by Zheng *et al.* [26]. In that case,  $\log \eta_{\infty}$  will be different for each of these three models.
2. It can be assumed that high-temperature viscosity limit ( $\log \eta_{\infty}$ ) is a truly universal value, independent of the model. (In the same way universality, independent of the model, was assumed for the fragility parameter  $m$ ). In this case, the parameter  $\eta_{\infty}$  would be the same and would have the same value:  $\log \eta_{\infty} \equiv \log \eta_{\infty M} = -1.93$  dPa·s for all three models.

Zheng *et al.* [26] presented the root mean square (RMS) error of the viscosity fit to 946 Corning compositions as a function of each composition, plotted from the highest to the lowest error. The MYEGA model provides the best fit with the lowest RMS error for the whole range of compositions, as compared to the VFT and AM models. For this reason, we selected the value  $\log \eta_{\infty} = -1.93$  dPa·s, which is calculated on the basis of the MYEGA model and proposed as universal. It should be noticed that the difference between the RMS error of the viscosity for the MYEGA and VFT models is subtle.

Our research goal is to find how the AM and VFT functions change within the given temperature interval in relation to whether they are calculated with an average or with a universal value of  $\eta_{\infty}$ . The question is to what extent the difference in values with each of them is significant. At the same time the aim is to determine whether it is possible to say which function is the best, i.e. which has the best correlation with the experimentally obtained results.

## II. Theoretical development

Our starting point is the fact that on the basis of the MYEGA model, the high temperature viscosity limit of silicate liquids  $\eta_{\infty M}$  is  $10^{-2.93}$  Pa·s [26]. Expressed in dPa·s, it is  $\log \eta_{\infty M} = -1.93$  dPa·s.

When expressed using the parameter  $\alpha$  characteristic for the AM model and assuming that the viscosity at  $T_r$  is  $10^{13}$  dPa·s, the MYEGA equation can be transformed into the following form [25]:

$$\log \eta_{MYEGA} = \log \eta_{\infty M} + (13 - \log \eta_{\infty M}) \frac{T_r}{T} \cdot \exp \left[ \left( \frac{17\alpha}{1.2(13 - \log \eta_{\infty M})} - 1 \right) \left( \frac{T_r}{T} - 1 \right) \right] \quad (4)$$

If  $\log \eta_{\infty M} = -1.93$  dPa·s is replaced into Eq. (4), the equation is transformed into:

$$\log \eta_{MYEGA} = -1.93 + 14.93 \frac{T_r}{T} \exp \left[ (0.95\alpha - 1) \left( \frac{T_r}{T} - 1 \right) \right] \quad (5)$$

It should be noted that for the referential temperature  $T_r$  viscosity is assumed to be always  $10^{13}$  dPa·s. According to the presented analysis Yue [27] states that there is an excellent correlation between the glass transition temperature  $T_g$  determined using the DSC method at the rate of 10 K/min and the temperature at which viscosity is  $\eta = 10^{13}$  dPa·s. Therefore, the referential temperature  $T_r$  is the same as the temperature assumed by Yue [27].

Let us analyse both possibilities, with different and the universal  $\eta_{\infty}$  values in the AM and VFT models.

### 2.1. Viscous flow equations with different $\eta_{\infty}$ values

#### The AM model

We start from the obtained result [26] that the average value of high-temperature viscosity limit in the AM model is  $\log \eta_{\infty A} = -0.74$  dPa·s. By substituting this value for  $\log \eta_{\infty A}$  in Eq. (2), it is transformed into the following equation:

$$\log \eta_{AM} = -0.74 + 13.74 \left( \frac{T_r}{T} \right)^{\alpha} \quad (6)$$

It should be mentioned that the AM model provides physically unrealistic high values of  $\eta_{\infty}$  for nearly all of the Corning compositions. This result follows directly from non-physical divergence of configurational entropy that has been predicted by the AM model. This divergence is physically unrealistic because only a finite number of configurations are available for any system. In contrast to the AM model, the VFT and MYEGA models correctly predict that configurational entropy is convergent for the high temperature limit.

#### The VFT model

The VFT equation can be expressed using the parameter  $\alpha$  characteristic for the AM equation and so transformed to obtain [25]:

$$\log \eta_{VFT} = 13 + (13 - \log \eta_{\infty V}) \frac{1 - \frac{T}{T_r}}{\frac{T}{T_r} + \frac{1.2}{\alpha} - 1} \quad (7)$$

This modification of the VFT equation is not quite trivial. We used result, obtained by Avramov [9], that, between  $T_0$  and  $T_r$  following relationship is fulfilled:  $T_0/T_r = 1 - 1.2/\alpha$ . In this way we eliminate the presence of temperature  $T_0$  in explicit form in the VFT equation. At present, there are some controversies regarding the physical meaning of  $T_0$  in the VFT equation. The VFT model predicts that at finite temperature  $T_0$  the configurational entropy becomes zero and it is considered a major deficiency of this model.

Assuming that  $\log \eta_{\infty v} = -2.87$  dPa·s, which is the average value of high-temperature viscosity limit for the VFT model [26], we obtain:

$$\log \eta_{VFT} = 13 + 15.87 \frac{1 - \frac{T}{T_r}}{\frac{T}{T_r} + \frac{1.2}{\alpha} - 1} \quad (8)$$

In contrast to the AM model, the VFT model produces comparatively low values of  $\eta_{\infty}$ . This is a by-product of non-physical divergence of viscosity at finite temperature  $T_0$  that is followed from the VFT function. In that way, all three equations for viscous flow are expressed through the parameter  $\alpha$  and the ratio  $T/T_r$ , so they can be compared directly.

### 2.2. Viscous flow equations with the universal $\eta_{\infty}$ values

We now assume that  $\log \eta_{\infty}$  has the same value for all three models, i.e.,  $\log \eta_{\infty} = -1.93$  dPa·s.

In that case, the expression for the viscous flow based on the MYEGA model remains the same (Eq. 5). The expressions for  $\log \eta$  based on the AM and the VFT models are obtained using  $\log \eta_{\infty} = -1.93$  dPa·s as a value for  $\log \eta_{\infty A}$  and  $\log \eta_{\infty v}$  in Eqs. 2 and 7, respectively. Therefore:

$$\log \eta_{AM} = -1.934 + 14.93 \left( \frac{T_r}{T} \right)^{\alpha} \quad (9)$$

$$\log \eta_{VFT} = 13 + 14.93 \frac{1 - \frac{T}{T_r}}{\frac{T}{T_r} + \frac{1.2}{\alpha} - 1} \quad (10)$$

Subtracting the right hand side of Eq. 9 from the right hand side of Eq. 6 we obtain the difference of viscosity by the AM model, depending whether the average value or the universal value of  $\log \eta_{\infty}$  is taken. The same is true for the VFT model, when we apply the same method for Eqs. 8 and 10. Therefore, the difference for the AM model is as follows:

$$\Delta \log \eta_{AM} = 1.19 - 1.19 \left( \frac{T_r}{T} \right)^{\alpha} \quad (11)$$

and for the VFT model:

$$\Delta \log \eta_{VFT} = 0.94 \frac{1 - \frac{T}{T_r}}{\frac{T}{T_r} + \frac{1.2}{\alpha} - 1} \quad (12)$$

For silicates it holds that  $\alpha = 1.2 + 6x$  [8,9].

We use the composition  $x$  meaning a “molar fraction” as defined by Avramov [8]. In that work, the silicates were considered as solution of  $(1 - x)$  molar fraction of  $\text{SiO}_2$  and the sum of molar fraction of other oxides ( $x$ ). For instance, the molar fraction of  $(\text{CaO})_{0.23}(\text{Al}_2\text{O}_3)_{0.15}(\text{SiO}_2)_{0.62}$  is  $x = 0.38$ . Relation  $\alpha = 1.2 + 6x$  is applicable for aluminosilicates containing also Ca and/or Mg, when composition (molar fraction)  $x$  is calculated in presented way. Taking this, for silicates the following equations are obtained:

$$\Delta \log \eta_{AM} = 1.19 - 1.19 \left( \frac{T_r}{T} \right)^{(1.2+6x)} \quad (13)$$

and

$$\Delta \log \eta_{VFT} = 0.94 \frac{1 - \frac{T}{T_r}}{\frac{T}{T_r} + \frac{1.2}{(1.2+6x)} - 1} \quad (14)$$

In most types of inorganic glasses direct covalent bonds exists, which form network and short-range ordering. But unlike crystals, the order does not exist at long distance. In the viscous flow of silicate glass-forming melts, two oxygen ions belonging to different though adjacent silicon ions exchange places. The result of this “switching of bends” is that oxygen exchange their host silicon ions [16].

### III. Testing of the obtained results

Both approaches presented above in subsections 2.1 and 2.2, were tested.

It is known that the thermal properties of multi-component silicate glasses, glass-ceramic materials and characteristics of silica liquids attract a great attention [28,29]. According to Zheng *et al.* [26] Corning glass liquids used for evaluating  $\eta_{\infty}$  values have some limited composition range.  $\text{SiO}_2$  was in the interval from about 58 mol% to 75 mol%. Additionally, the authors tested 31 other liquids including metallic, molecular and ionic systems, although data concerning composition range of these liquids are not clearly defined. In this work we take into consideration only 6 systems, but they cover much wider composition range of  $\text{SiO}_2$  than in work done by Zheng *et al.* [26]. The composition range that has been taken into account to discuss the universality of

**Table 1. Materials, referential temperature  $T_r$  (obtained from cited experimental data), molar fraction  $x$  and fragility parameter  $\alpha$**

Material	$T_r$ [K]	$x$	$\alpha$	Ref.
$(\text{CaO})_{0.25}(\text{MgO})_{0.25}(\text{SiO}_2)_{0.5}$	996.3	0.500	4.200	[30]
$(\text{CaO})_{0.25}(\text{Al}_2\text{O}_3)_{0.25}(\text{SiO}_2)_{0.5}$	1133.0	0.500	4.200	[30]
$(\text{CaO})_{0.44}(\text{Al}_2\text{O}_3)_{0.44}(\text{SiO}_2)_{0.12}$	1140.1	0.880	6.480	[30]
$(\text{Na}_2\text{O})_{0.125}(\text{Al}_2\text{O}_3)_{0.125}(\text{SiO}_2)_{0.75}$	1096.0	0.250	2.700	[30]
$(\text{CaO})_{0.11}(\text{Al}_2\text{O}_3)_{0.12}(\text{SiO}_2)_{0.77}$	1153.0	0.230	2.580	[30]
$(\text{CaO})_{0.376}(\text{SiO}_2)_{0.624}$	1064.4	0.376	3.456	[8]

the  $\eta_\infty$  was from 0.12 mol% to 77 mol% of SiO<sub>2</sub> including materials in the middle of this interval with 50 mol% of SiO<sub>2</sub>.

The particular systems that are used for testing are listed in Table 1 with corresponding data for referential temperature  $T_r$ , molar fraction  $x$  and fragility parameter  $\alpha$  that were used for calculating viscosity. The presented referential temperatures  $T_r$ , have been obtained by extrapolation experimental data. These temperatures differ less than 3% from data for  $T_g$  which are given by Sipp *et al.* [30]. For (CaO)<sub>0.376</sub>(SiO<sub>2</sub>)<sub>0.624</sub>, the value of referential temperature  $T_r = 1064.4$  K has been obtained using the expression  $T_r(L) = T_{gSiO_2} / [1.26 + 3.6L(1-L)]T_r$  and data  $T_{gSiO_2} = 1435$  K and  $L = 0.030$  [8].

The present study performs testing of the obtained results for 6 particular compositions. This amount is not enough to decide, which of the models will always give the best results and which of them would have the priority in prediction comparing to the other two models. But this number of materials, that have a different composition, will be sufficient to detect differences if they exist by applying these three models.

The selected silicate liquids may show different characteristics on viscosity, for example lubricant effect for (CaO)<sub>0.376</sub>(SiO<sub>2</sub>)<sub>0.624</sub> and the charge compensation effect of Al<sup>3+</sup> cation for (Na<sub>2</sub>O)<sub>0.125</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>0.125</sub>(SiO<sub>2</sub>)<sub>0.75</sub>. This diversity of materials is useful, because we have the possibility to observe behaviour of the three models in situations with possibly different viscous characteristics.

Figures 1a,b show the 3D diagrams of the differences  $\Delta \log \eta_{AM}$  and  $\Delta \log \eta_{VFT}$  between the values of the functions obtained when we use the average and universal  $\eta_\infty$  for temperature ratio  $1 \leq T/T_r \leq 2$  and in a wide range of  $x$ . Analogous 3D diagrams of the differences  $\Delta \log \eta_{AM}$  and  $\Delta \log \eta_{AM}$  for temperature ratio  $1 \leq T/T_r \leq 1000$  are presented in Figs. 1c,d, respectively. Figure 1 is obtained according to Eqs. 13 and 14.

Figure 2a presents viscosity curves of (CaO)<sub>0.11</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>0.12</sub>(SiO<sub>2</sub>)<sub>0.77</sub> obtained from the AM model with the average and the universal values  $\eta_\infty$ , that is from Eqs. 6 and 9 respectively as well as the experimental viscosity curve on the basis of the data from [30]. Figure 2b presents viscosity curves of the same material obtained for the VFT model with the average and the universal values  $\eta_\infty$ , that is from Eqs. 8 and 10, respectively, together with the mentioned experimental curve. The results of our testing on the systems (CaO)<sub>0.376</sub>(SiO<sub>2</sub>)<sub>0.624</sub> are presented in Fig. 3. This material is an example of a system with a weak lubricant effect. The curves in Fig. 3a are obtained from Eqs. 6 and 9 for the AM model with the average and the universal values of  $\log \eta_\infty$ . The analogous curves for the VFT model on Fig. 3b were calculated on the basis of Eqs. 8 and 10. In both cases the data for the experimental curves are taken from the reference [31].

Figures 4a,b show the viscous functions for (CaO)<sub>0.25</sub>(MgO)<sub>0.25</sub>(SiO<sub>2</sub>)<sub>0.5</sub> and

(CaO)<sub>0.25</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>0.25</sub>(SiO<sub>2</sub>)<sub>0.5</sub>, respectively, obtained from the AM, VFT and MYEGA model with the universal value of  $\log \eta_\infty$ , that is based on Eqs. 9,10 and 5. The experimental curves in these figures are obtained on the basis of the data from [30].

Table 2 presents the values of standard error of the estimate (*SEE*) for the functions calculated on the basis of the equations presented in sections 2.1 and 2.2 in comparison to the experimental values for the tested materials.

The standard error of the estimate is a measure of the accuracy of predictions. It is expressed generally as:

$$SEE = \sqrt{\frac{\sum (Y_{ical} - Y_{iexp})^2}{N - 2}} \quad (15)$$

where  $Y_{ical}$  is estimated (calculated) value,  $Y_{iexp}$  is experimental value and  $N$  is number of observations. In our case, the *SEE* was calculated as:

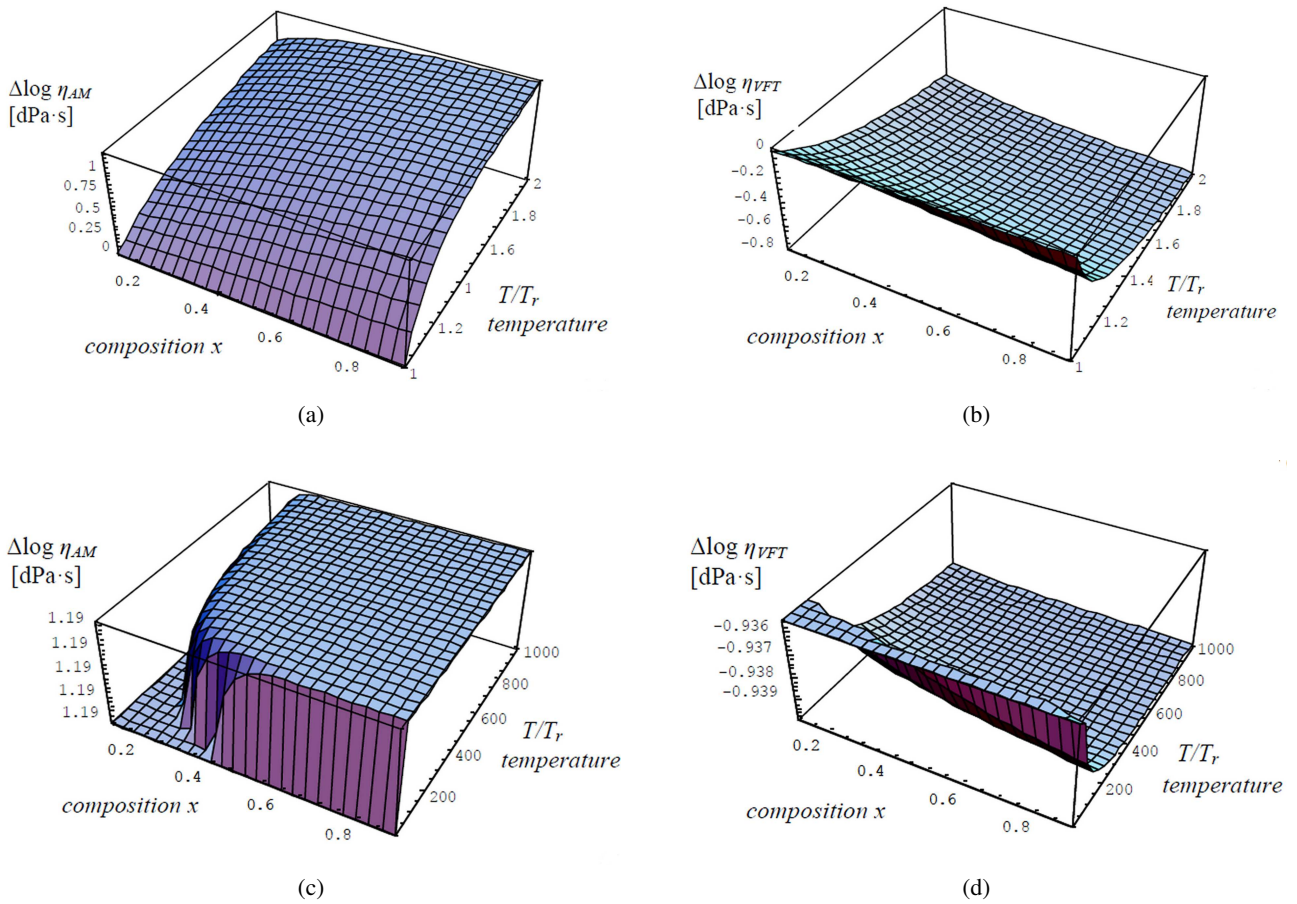
$$SEE = \sqrt{\frac{\sum (\log \eta_{ical} - \log \eta_{iexp})^2}{N - 2}} \quad (16)$$

where  $\log \eta_{iexp}$  is experimental value of viscosity and  $\log \eta_{ical}$  is calculated value of viscosity by the given model at the same temperature. The temperature range, where the numbers of observations  $N$  for these calculations belong, was different (this range depends on the material). Generally, the minimal temperature that appears was 969 K, and maximal 2449 K. The number of observations  $N$  that was used for calculations of *SEE* varied from 23 to 33.

#### IV. Discussion

Figure 1 shows the 3D diagrams of the difference between the values of the function for a given model, in the case when they are calculated with the average and with the universal  $\log \eta_\infty$ .

Results shown in Figs. 1a,b are included to that in Figs. 1c,d, respectively, although it seems that these results do not correspond to each other. The reason for this is a difference in the range of  $T/T_r$  that was shown in these figures. Figures 1c,d which include very high temperatures, cover a wider temperature range. As a result of that, they roughly represent what happens with the differences of viscosity functions. On the other hand, Figs. 1a,b present a focused view in the narrow temperature interval around  $T_r$ . Figures 1c,d do not have such a good “resolution” to be able to show this with all details. From Figs. 1a,b, it is obvious that in the case  $T/T_r > 2$  the values of  $\Delta \log \eta$  will be higher than 1.0 and smaller than  $-0.8$  for the AM and VFT model, respectively. Because the interval of  $T/T_r$  presented in Figs 1c,d is up to  $T/T_r = 1000$ , these values of  $\Delta \log \eta$  are achieved at the very beginning of the  $T/T_r$  axis. As a result, the ordinate axes in these figures begin with the values that are higher than 1.0 and smaller than  $-0.8$ . It should be men-



**Figure 1.** Differences  $\Delta \log \eta$  in dPa·s obtained by using Eq. 13 for AM and Eq. 14 for VFT model. (a)  $\Delta \log \eta_{AM}$  when  $T/T_r$  is in the range from 1 to 2; (b)  $\Delta \log \eta_{VFT}$  when  $T/T_r$  is in the range from 1 to 2; (c)  $\Delta \log \eta_{AM}$  when  $T/T_r$  is in the range from 1 to 1000; (d)  $\Delta \log \eta_{VFT}$  when  $T/T_r$  is in the range from 1 to 1000, where  $T_r$  is the referential temperature at which the viscosity is  $10^{13}$  dPa·s

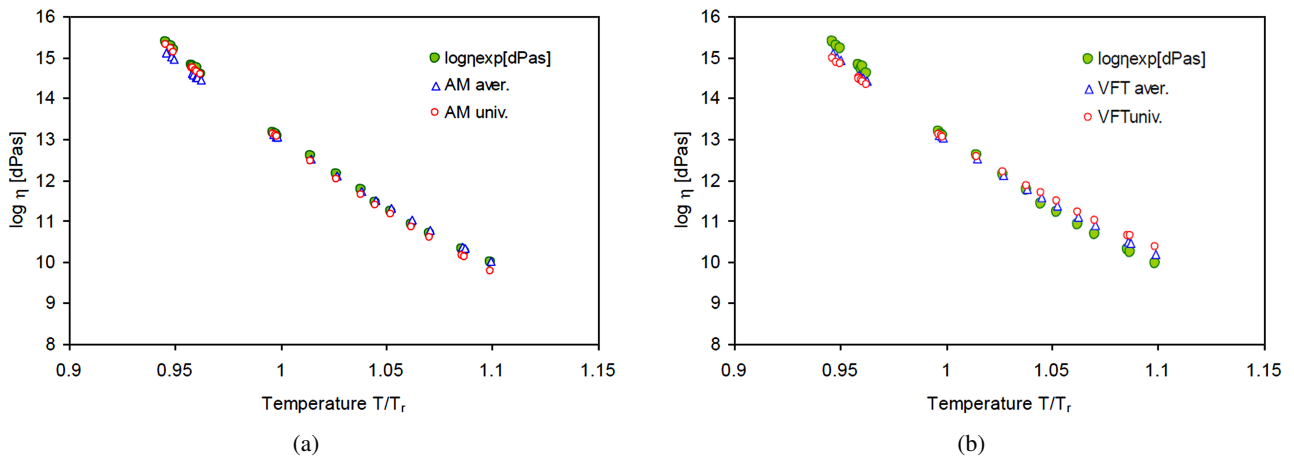
tioned that the value of 1.19 is indicated along whole ordinate axis in Fig. 1c, because differences between the  $\Delta \log \eta_{AM}$  values appear only at further decimals and program for calculation does not present them.

As it can be seen from Figs. 1a,b, the values of the AM function will depend to a larger extent on whether the average or the universal value for  $\eta_\infty$  is taken than in the case of the VFT function. For both models, however, in the temperature interval  $1 < T/T_r < 1.2$ , it is less important which  $\eta_\infty$  has been taken for calculation. It is evident that in this temperature interval the differences  $\Delta \log \eta$  are small and their dependence on composition  $x$  is negligible for both models.

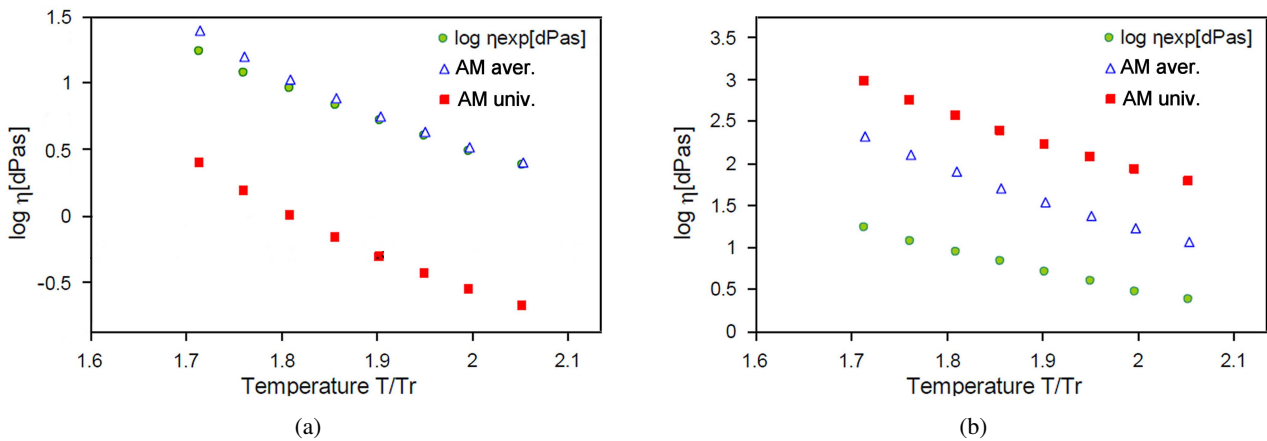
With the increase of temperature and  $x$ , the absolute values of  $\Delta \log \eta$  will increase for both models. The AM function will have higher values with the average  $\log \eta_\infty$  than for the universal one, but for the VFT model we have the opposite case. When the temperature is increased further (Figs. 1c,d) the values of  $\Delta \log \eta$  for both models will be the differences between the average and the universal value of  $\log \eta_\infty$ . This follows directly from Eqs. 11 and 12, where  $\Delta \log \eta$  for  $T \rightarrow \infty$  will have values 1.19 and  $-0.94$  for the AM and VFT model, respectively.

Figures 2 and 3 show the dependency of  $\log \eta$  on  $T/T_r$  for  $(\text{CaO})_{0.11}(\text{Al}_2\text{O}_3)_{0.12}(\text{SiO}_2)_{0.77}$  and  $(\text{CaO})_{0.376}(\text{SiO}_2)_{0.624}$ , respectively. These figures show that with the AM model the values of  $\log \eta$  are higher if calculated with the average values of  $\log \eta_\infty$  than with the universal values when  $T/T_r \geq 1$ . If the VFT model is applied, the situation is the opposite. As it was mentioned above, this was correctly predicted by the 3D diagrams in Fig. 1. It is obvious from Figs. 2a,b that the values of  $\log \eta$  for  $(\text{CaO})_{0.11}(\text{Al}_2\text{O}_3)_{0.12}(\text{SiO}_2)_{0.77}$  for each of the models separately, are highly similar, regardless of whether they are calculated with the average or the universal values of  $\log \eta_\infty$ . On the graphs in Figs 2a,b the ratio of temperature  $T/T_r$  was up to 1.1. The 3D diagrams from Fig. 1 also predicted that in the temperature interval  $1 < T/T_r < 1.2$ , for both models it is less important which  $\eta_\infty$  has been taken for calculation.

A completely different situation is observed in Figs 3a,b which represent viscous functions for  $(\text{CaO})_{0.376}(\text{SiO}_2)_{0.624}$ . There is a weak lubricant effect with these alloys. As it was mentioned by Avramov [8] a very small amount of network modifiers added to pure  $\text{SiO}_2$  can cause a drastic decrease of viscosity



**Figure 2. Viscosity curves of  $(\text{CaO})_{0.11}(\text{Al}_2\text{O}_3)_{0.12}(\text{SiO}_2)_{0.77}$  obtained from: (a) the AM model with the average value of  $\log \eta_{\infty A}$  (Eq. 6) and with the universal value of  $\log \eta_{\infty}$  (Eq. 9); (b) the VFT model with the average value of  $\log \eta_{\infty V}$  (Eq. 8) and with the universal value of  $\log \eta_{\infty}$  (Eq. 10). The plot of  $\log \eta_{\text{exp}}$  in [dPa·s] is based on the data from [30].  $T_r$  is the referential temperature at which the viscosity is  $10^{13}$  dPa·s**



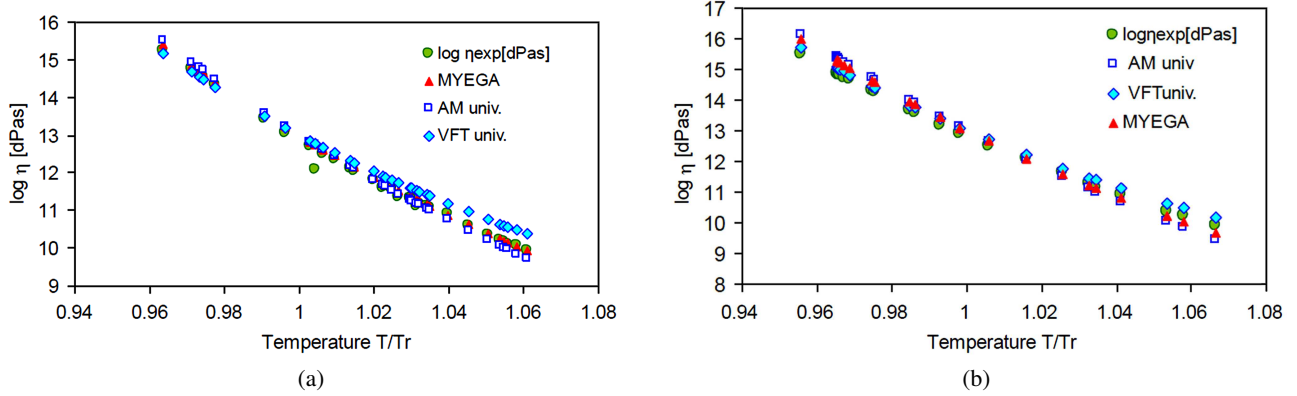
**Figure 3. The viscosity curves of  $(\text{CaO})_{0.376}(\text{SiO}_2)_{0.624}$  obtained from: (a) the AM model with the average value of  $\log \eta_{\infty A}$  (Eq. 6) and with the universal value of  $\log \eta_{\infty}$  (Eq. 9); (b) the VFT model with the average value of  $\log \eta_{\infty V}$  (Eq. 8) and with the universal value of  $\log \eta_{\infty}$  (Eq. 10). The plot of  $\log \eta_{\text{exp}}$  in [dPa·s] is based on the data from [31].  $T_r$  is the referential temperature at which the viscosity is  $10^{13}$  dPa·s**

at the temperature equivalent to the  $T_g$  of pure  $\text{SiO}_2$ . It was shown [8] that the effect of a lubricant can be calculated by introducing lubricant coefficient  $k_i$  whose values are between 0 and 1 and lubricant molar fraction  $L_i = x_i k_i$ . Total lubricant fraction is  $L = \sum L_i$ . In this way the decrease of  $T_r$  influenced by lubricants with silicates can be represented with good approximation by equation  $T_r(L) = T_{g(\text{SiO}_2)} / [1.26 + 3.6L(1 - L)]$ . With  $(\text{CaO})_{0.376}(\text{SiO}_2)_{0.624}$  it holds that  $k = 0.08$  and  $x = 0.376$  (i.e.  $L = 0.030$ ) [8]. Figure 3 shows viscous functions for the temperature interval  $1.7 < T/T_r < 2.1$ . As it can be seen from Fig. 1, in that range of  $T/T_r$  the differences in the values of the AM and VFT functions taken separately are much larger than in the temperature range which is about  $T_r$ . According to the 3D diagram, the values of  $\eta$  for the AM model when calculated with  $\log \eta_{\infty A} = -0.74$  dPa·s and with  $\log \eta_{\infty} = -1.93$  dPa·s differ for about one order of magnitude. With the VFT

model the differences are somewhat smaller and more dependent on composition  $x$ . For  $(\text{CaO})_{0.376}(\text{SiO}_2)_{0.624}$  the differences are  $1.005 < \Delta \log \eta_{\infty AM} < 1.091$  and  $-0.707 < \Delta \log \eta_{\infty VFT} < -0.632$  for the given interval  $T/T_r$ .

Another question relates to the extent to which the calculated viscous functions agree with the experimentally obtained results.

From Figs. 2b and 4a it is obvious that the values of the VFT function, which are calculated with the universal value of  $\log \eta_{\infty}$  within the range of low viscosity, differ from the measured ones for almost one order of magnitude. The same has been implied from Figs. 3a and 4b for AM functions calculated with the universal value of  $\log \eta_{\infty}$ . In all these cases, the slope of calculated curves becomes slightly different in comparison with the slope of experimental ones. Therefore, we can conclude that the VFT and AM functions, calculated with the



**Figure 4.** The viscosity curves of: (a)  $(\text{CaO})_{0.25}(\text{MgO})_{0.25}(\text{SiO}_2)_{0.5}$  and (b)  $(\text{CaO})_{0.25}(\text{Al}_2\text{O}_3)_{0.25}(\text{SiO}_2)_{0.5}$  obtained on the basis of Eqs 9,10,5 for the AM, the VFT and the MYEGA model, respectively. The plot of experimental curves  $\log \eta_{\text{exp}}$  in [dPa·s] is based on the data from [30].  $T_r$  is the referential temperature at which the viscosity is  $10^{13}$  dPa·s

**Table 2.** The standard error of estimate (*SEE*) for the functions calculated on the basis of the equations from section 2 in relations to experimental values for the tested materials

Material	<i>SEE</i> for AM	<i>SEE</i> for AM	<i>SEE</i> for VFT	<i>SEE</i> for VFT	<i>SEE</i> for
	$\eta_{\infty}$ average	$\eta_{\infty}$ universal	$\eta_{\infty}$ average	$\eta_{\infty}$ universal	MYEGA
$(\text{CaO})_{0.25}(\text{MgO})_{0.25}(\text{SiO}_2)_{0.5}$	0.159	0.177	0.233	0.314	0.152
$(\text{CaO})_{0.25}(\text{Al}_2\text{O}_3)_{0.25}(\text{SiO}_2)_{0.5}$	0.236	0.387	0.238	0.208	0.289
$(\text{CaO})_{0.44}(\text{Al}_2\text{O}_3)_{0.44}(\text{SiO}_2)_{0.12}$	0.489	0.685	0.45	0.35	0.56
$(\text{Na}_2\text{O})_{0.125}(\text{Al}_2\text{O}_3)_{0.125}(\text{SiO}_2)_{0.75}$	0.666	0.851	0.604	0.498	0.734
$(\text{CaO})_{0.11}(\text{Al}_2\text{O}_3)_{0.12}(\text{SiO}_2)_{0.77}$	0.147	0.103	0.203	0.303	0.096
$(\text{CaO})_{0.376}(\text{SiO}_2)_{0.624}$	0.097	1.138	1.206	1.789	0.118

universal value of high temperature viscosity limit are less applicable. On the other hand, Fig. 3 shows that the good agreement with experimental curves appears with the AM function calculated with average value of  $\log \eta_{\infty}$ . In contrast to this, both calculated VFT functions as well as the AM function which is calculated with the universal value  $\log \eta_{\infty}$ , are shifted along the vertical axis and differ in relation to the measured values in the whole range of low viscosity.

Table 2 gives the values of *SEE* which indicate the agreement of the AM and the VFT functions, calculated with the average and the universal value of  $\log \eta_{\infty}$ , in relation to the experimental functions. It also gives the values of *SEE* agreement of the MYEGA function calculated according to Eq. 5. As it can be seen from Table 2 it is not possible to say which of the analysed functions shows the best agreement with the experimental one and which will always give the lowest value of *SEE*.

From Fig. 3 and from data in Table 2 for  $(\text{CaO})_{0.376}(\text{SiO}_2)_{0.624}$ , it is obvious that calculated viscosities with the use of average values of  $\eta_{\infty}$  are closer to the experimental results than those with the use of universal  $\eta_{\infty}$  value, no matter whether the AM or VFT model is used. Therefore, it may be suggested that the average  $\eta_{\infty}$  value should be used for each model rather than the universal  $\eta_{\infty}$  values for precise predictions of viscosity. But, as presented in Table 2, it is not possible to say that analysed functions, if calcu-

lated with average values of  $\eta_{\infty}$ , will always give the best agreement with the experimental one. For example, *SEE* of VFT functions, which are calculated with universal value of  $\eta_{\infty}$  for  $(\text{CaO})_{0.25}(\text{Al}_2\text{O}_3)_{0.25}(\text{SiO}_2)_{0.5}$  and  $(\text{Na}_2\text{O})_{0.125}(\text{Al}_2\text{O}_3)_{0.125}(\text{SiO}_2)_{0.75}$  are smaller than *SEE* of VFT functions with average value of  $\eta_{\infty}$ . This also holds for AM functions in case of  $(\text{CaO})_{0.11}(\text{Al}_2\text{O}_3)_{0.12}(\text{SiO}_2)_{0.77}$ . For this material, *SEE* for AM function when calculated with average value of  $\eta_{\infty}$  is 0.147, while *SEE* with universal value of  $\eta_{\infty}$  is 0.103.

The lowest values of *SEE* with materials from Table 2 are obtained for  $(\text{CaO})_{0.11}(\text{Al}_2\text{O}_3)_{0.12}(\text{SiO}_2)_{0.77}$  calculated with the MYEGA function (0.096). A similar value (0.097), is obtained for  $(\text{CaO})_{0.376}(\text{SiO}_2)_{0.624}$  with the AM function when it is calculated with the average value  $\log \eta_{\infty}$ . On the other hand, with  $(\text{CaO})_{0.376}(\text{SiO}_2)_{0.624}$  we also observe the highest *SEE* value of 1.789, obtained when the VFT function is calculated with the universal value of  $\log \eta_{\infty}$ .

From Table 2, it is obvious that for the melts  $(\text{CaO})_{0.44}(\text{Al}_2\text{O}_3)_{0.44}(\text{SiO}_2)_{0.12}$  and  $(\text{Na}_2\text{O})_{0.125}(\text{Al}_2\text{O}_3)_{0.125}(\text{SiO}_2)_{0.75}$  the values of *SEE* are high, regardless of model and the use of the average or universal  $\eta_{\infty}$  value. The material  $(\text{CaO})_{0.44}(\text{Al}_2\text{O}_3)_{0.44}(\text{SiO}_2)_{0.12}$  does not belong to the composition range considered in [26], where the universality of the high-temperature viscosity



limit was introduced. Therefore, for this material the proposed universal and average values of  $\eta_\infty$  are probably not appropriate and should be corrected. Also, the charge compensation effect of  $\text{Al}^{3+}$  cation for  $(\text{Na}_2\text{O})_{0.125}(\text{Al}_2\text{O}_3)_{0.125}(\text{SiO}_2)_{0.75}$  probably requires the introduction of additional correction in calculation of the  $\eta_\infty$  values.

In case of  $(\text{CaO})_{0.376}(\text{SiO}_2)_{0.624}$ , the high value of  $SEE$  for the VFT model is obtained, regardless whether we use the average or universal value of  $\eta_\infty$ . The VFT model was derived empirically, but justifications of this model are based on estimation of the average activation energy. Instead of the average energy barrier, the AM model considers the average jump frequency of the building units responsible for the viscous flow [4–6]. As a result, the main difference of the two approaches appears for materials when the small amount of impurity is added to pure  $\text{SiO}_2$ . From Table 2 follows that the VFT model is less reliable in prediction of lubricant effect regardless which value of  $\eta_\infty$  is used. On the other hand, calculated  $SEE$  for the AM model, with average value of  $\eta_\infty$  and for the MYEGA model, have the satisfactory values. However, when the lubricant effect is calculated with the universal  $\log \eta_\infty$  value, the AM model shows inaccurate results. Therefore, for precise prediction of viscosity in materials with lubricant effect it is important which model and which value of  $\eta_\infty$  is used in calculations.

It can be noticed from Table 2 that the differences in the values of  $SEE$  in relation to whether the functions are calculated with the average or the universal  $\log \eta_\infty$ , are the greatest with  $(\text{CaO})_{0.376}(\text{SiO}_2)_{0.624}$ . This is understandable and also in accordance with the predictions of the 3D diagram in the case where  $T/T_r > 1.2$ . With other materials we do not encounter such big differences in the values of  $SEE$  in relation to whether the calculation was done with the average or the universal high temperature viscosity. It is important to emphasize that in these cases the temperature interval under consideration is closer to  $T_r$ . For that reason, in this restricted  $T/T_r$  interval, if the experimental function showed good agreement with the function calculated with the average high temperature viscosity limit, it also shows good agreement with the one calculated with the universal  $\log \eta_\infty$ . Unlike Fig. 2 which shows the functions with both the average and the universal  $\log \eta_\infty$ , Fig. 4 shows all three viscous functions calculated only with the universal  $\log \eta_\infty$ . As we have found, in the interval  $1 < T/T_r < 1.2$  the functions calculated with the average high temperature viscosity limit will behave in the similar way. It can be seen in Fig. 4b that for  $(\text{CaO})_{0.25}(\text{Al}_2\text{O}_3)_{0.25}(\text{SiO}_2)_{0.5}$  all three functions show quite good agreement with the experimental curve. It is also observed from Fig. 4a that for  $(\text{CaO})_{0.25}(\text{Al}_2\text{O}_3)_{0.25}(\text{SiO}_2)_{0.5}$  with the increase in temperature, the VFT begins to show greater deviations. However, a general statement that the VFT function gives the worst results cannot be made. It can be

seen from Table 2 that when the  $SEE$  values at each of these materials are compared for the three models tested here, sometimes the  $SEE$  for the MYEGA is the lowest, sometimes the  $SEE$  for the VFT is the lowest and sometimes it is for the AM function. Therefore, for  $(\text{CaO})_{0.25}(\text{Al}_2\text{O}_3)_{0.25}(\text{SiO}_2)_{0.5}$  it is the VFT which shows the best correlation with the experimental results (Fig. 4b and Table 2) when calculated with the universal  $\log \eta_\infty$ .

## V. Conclusions

3D diagrams can successfully predict the difference in behaviour of viscous functions when average and universal high temperature limit is applied in calculations. The values of the AM functions are more affected by the choice of whether to take the average or the universal value for  $\eta_\infty$  than it is the case with the VFT model. In the temperature interval  $1 < T/T_r < 1.2$  for both models it is less important which  $\eta_\infty$  has been taken for calculations. The differences between the values of viscous functions are more significant for higher temperatures in relation to referential  $T_r$ .

It can be concluded that the MYEGA function proved to be just as successful as the AM function in predicting the lubricant effect and showed good agreement with the experimental results.

The test and values of standard error of estimate ( $SEE$ ) show that there are no general rules whether the average or universal high temperature viscosity limit should be taken to get the best agreement with the experimental functions.

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