

INCLUSION OF P_2O_5 AND VO_x IN THE VISCOSITY MODEL FOR MOLTEN SLAG IN MULTICOMPONENT OXIDE SYSTEMS

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Introduction

Knowledge of slag viscosity is important to understand the physical and thermochemical processes in many industrial applications, for example in coal or biomass entrained-flow gasifiers. In the framework of the HotVeGas and HViGasTech projects, a structure-based viscosity model¹⁻³ has recently been developed for the fully liquid system $SiO_2-Al_2O_3-CaO-MgO-Na_2O-K_2O-FeO-Fe_2O_3$. In this work, the model will be extended to describe the viscosity contribution from the components P_2O_5 and VO_x , which are often contained in coal or biomass slags. The challenges for the model extension will be discussed. The model performance will be demonstrated using some low-order systems.

The viscosity model

The idea for the viscosity modelling is to correlate the viscosity to the internal structure of molten slags. Description of the structure is based on a self-consistent thermodynamic database, where the non-ideal associate solution is used to describe the molten slag. The associate species are assumed to indicate structural units in molten slags. The associate species distribution is then used to describe the structural change induced by temperature, composition and atmosphere. The viscosity contribution of each associate species can be described by the Arrhenius model. It was reported that some associate species such as SiO_2 and $NaSiAlO_4$ can generate larger structural units (*i.e.* clusters) through self- or inter-polymerisation, and cause an increased viscosity.^{1,2} In order to adequately describe the viscosity contribution, two viscosity parts, *i.e.* an ideal part and an excess part are proposed, which has been described in more detail elsewhere¹⁻³. The viscosity equation for P_2O_5 - or VO_x -containing low-order systems reads:

$$\ln \eta = \ln \eta_{\text{ideal}} + \ln \eta_{\text{excess}} = (\sum X_i \cdot \ln \eta_i) + (\ln \eta_{\text{self-pol.}}) \quad (1)$$

where: $\ln \eta_i = A_i + B_i/T$

$$\ln \eta_{\text{self-pol.}} = \sum (A_j + B_j/T) \cdot (X_j)^n$$

i: monomeric associate species

j: network former

η_{ideal} is the ideal part based on the assumption that each associate species is a discrete structural unit without any polymerisation; η_{excess} is the excess part, which here refers to $\eta_{\text{self-pol.}}$, resulting from the formation of clusters; X_i is the mole fraction of the monomeric associate species i; A_i , A_j , B_i and B_j are the temperature- and composition-independent constants; T is the absolute temperature; n is the integer coefficient that relates to a particular degree of polymerisation; $(X_j)^n$ is the weighting factor referring to the contribution of additional clusters.

Results and discussion

The assessment of the model parameters requires sufficient reliable experimental data. For P_2O_5 - and VO_x -containing systems, only few data are available in the literature. In order to better optimise the model parameters, boundary conditions regarding the bond strength and structural information are set.

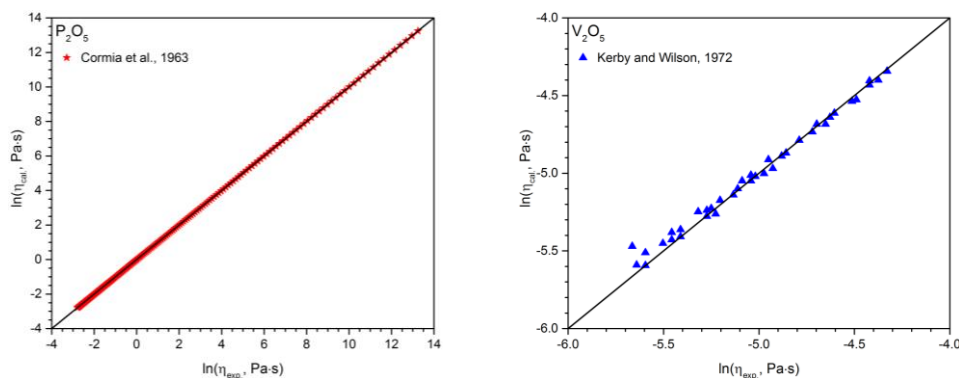


Figure 1: Comparison between experimental data and calculated viscosities for pure P_2O_5 and V_2O_5

Figure 1 shows that the calculated viscosities of pure P_2O_5 are in agreement with the experimental data⁴. However, P_2O_5 behaves as a network former, whose natural logarithmic viscosity values cover more than 12 orders of magnitude (see Figure 1). Therefore, the treatment of the viscosity of P_2O_5 should be similar to that of SiO_2 . One additional cluster $(\text{PO}_{2.5})_{20}$ resulting from the self-polymerisation is introduced to describe the structural feature in pure P_2O_5 melt. Here, the polymerisation degree of 20 is the result of fitting the experimental data for the pure oxide and relevant binary systems. Without the polymerisation, the viscosities extrapolated from pure oxide to binary systems or to higher order systems exhibit large deviations.

The treatment of VO_x -induced structural change is similar to that of FeO_x . The structural features of VO_x melts are described by the distribution of the species VO , V_2O_3 , VO_2 and V_2O_5 calculated from a self-consistent thermodynamic database, where a non-ideal associate solution is used to describe the temperature, composition and oxygen partial pressure dependence of the Gibbs-energy of molten oxides. The model reproduces the data⁵ measured at oxygen partial pressures of 0.1–0.5 bar (see Figure 1). The low magnitude of viscosity values implies that no additional clusters are required for VO_x -containing systems, although V_2O_5 is an analogue of P_2O_5 ⁶.

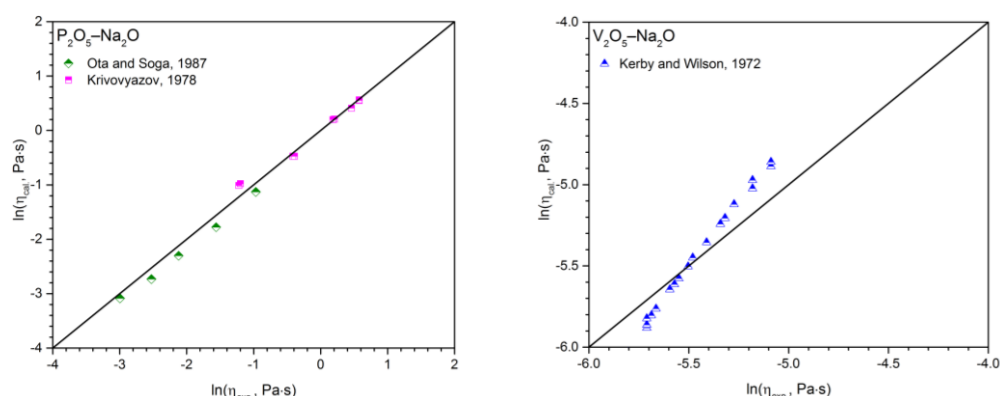


Figure 2: Comparison between experimental data and calculated viscosities in the systems $\text{P}_2\text{O}_5\text{--Na}_2\text{O}$ and $\text{V}_2\text{O}_5\text{--Na}_2\text{O}$

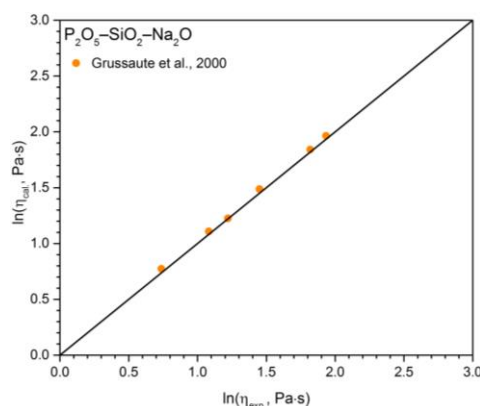


Figure 3: Comparison between experimental data and calculated viscosities in the system $\text{P}_2\text{O}_5\text{--SiO}_2\text{--Na}_2\text{O}$

Based on the monomeric associate species Na_2O , P_2O_5 , NaPO_3 , Na_3PO_4 and $\text{Na}_4\text{P}_2\text{O}_7$ in combination with one additional cluster $(\text{PO}_{2.5})_{20}$, the experimental data^{7,8} are reproduced in the system $\text{P}_2\text{O}_5\text{--Na}_2\text{O}$, as shown in Figure 2. To further evaluate the model performance, the model is extended to higher order systems, for example to the ternary system $\text{P}_2\text{O}_5\text{--SiO}_2\text{--Na}_2\text{O}$, where besides the clusters employed for related binary systems no additional clusters are employed to reproduce the experimental viscosities⁹, as shown in Figure 3. With the same approach, the viscosity of the system

V_2O_5 – Na_2O is calculated, although some deviations occur compared to the experimental data⁵ (see Figure 2). It is noted that the thermodynamic database for VO_x -containing systems is still being developed and the associate species distribution used in this work could be improved in the future.

Conclusion

The structure-based model can adequately describe the influence of the components P_2O_5 and VO_x on slag viscosity in low-order systems. To improve the model performance, the P_2O_5 - and VO_x -induced viscosity behaviour should be correlated to the structural change with caution. Some additional clusters may need to be introduced due to the potential interconnection of relevant associate species. The model parameters should be further assessed when new reliable experimental data are available.

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