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Thermodynamic model and viscosity of Na_2O–MgO–CaO–SiO_2 glasses

Mária Chromčíková [a,*], Marek Liška [a], Jan Macháček [b], Jozef Chovanec [c]

[a] Vitrum Laugaricio, Joint Glass Center of IIC SAS, TnU AD, RONA, and FChPT STU, SK-911 50 Trenčín, Slovakia
[b] Institute of Chemical Technology Prague, Technická 5, Prague CZ-166 28, Czech Republic
[c] Department of Physical Chemistry, Faculty of Chemical Technology, University of Pardubice, CZ-532 10 Pardubice, Czech Republic

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ABSTRACT

The structure–viscosity relationship of $15Na_2O{\cdot}xMgO{\cdot}(10-x)CaO{\cdot}75SiO_2$ ($x = 0, 2, 4, 6, 8, 10$) glasses was studied. The structure of studied glasses was described by the thermodynamic model of Shakhmatkin and Vedishcheva. Thermodynamic modeling resulted in eight components with significant abundance in the studied glasses, i.e. SiO_2, $2MgO{\cdot}SiO_2$, $MgO{\cdot}SiO_2$, $Na_2O{\cdot}3CaO{\cdot}6SiO_2$, $Na_2O{\cdot}CaO{\cdot}5SiO_2$, $Na_2O{\cdot}MgO{\cdot}4SiO_2$, $Na_2O{\cdot}SiO_2$ and $Na_2O{\cdot}2SiO_2$. Due to significant positive correlations between equilibrium molar amounts of ($2MgO{\cdot}SiO_2$–$MgO{\cdot}SiO_2$), ($Na_2O{\cdot}3CaO{\cdot}6SiO_2$–$Na_2O{\cdot}CaO{\cdot}5SiO_2$), ($Na_2O{\cdot}MgO{\cdot}4SiO_2$–$Na_2O{\cdot}SiO_2$), and ($Na_2O{\cdot}SiO_2$–$Na_2O{\cdot}2SiO_2$) only four significant components were considered in the regression treatment, namely SiO_2, $MgO{\cdot}SiO_2$, $Na_2O{\cdot}3CaO{\cdot}6SiO_2$, and $Na_2O{\cdot}2SiO_2$. The experimental viscosity data obtained in the viscosity range from 10^2 dPa·s to 10^{12} dPa·s were alternatively described by various commonly used viscosity equations — Adam and Gibbs, Avramov and Milchev, and MYEGA. The compositional dependence of parameters of the above viscosity equations was described by multi-linear formulas taking as independent variables the equilibrium molar amounts of significant components of the thermodynamic model. The statistical analysis of the non-linear regression results was performed and only the statistically significant members were retained in the multi-linear forms. The assumption of composition independent high temperature viscosity limit was checked for all used viscosity equations. It was found that statistically equivalent description of experimental data is obtained by supposing the compositional dependence of this quantity. It was statistically confirmed that when the system composition is described by molar amounts of true components obtained from proper thermodynamic model the compositional dependence of parameters of considered viscosity equations acquires the simple multilinear linear form.

1. Introduction

The viscosity of silicate glasses belongs to the most important properties both from the technological and theoretical points of view [1–3]. The compositional dependence of physical properties of oxide glasses is commonly treated by multilinear regression where the molar/weight fractions of individual oxides are used as independent variables [4]. However such models despite their common use in the glass technology cannot be applied outside the compositional range of experimental values used in the regression treatment. On the other side, the thermodynamic models posses the possibility for obtaining more realistic models enabling in some extent also the extrapolation [3]. Therefore the present work deals with the application of Shakhmatkin and Vedishcheva thermodynamic model for interpretation of viscosity–temperature relationship as a function of composition in the case of Na_2O–MgO–CaO–SiO_2 glasses. The main aim of the present work is to confirm, that when the system composition is described by molar amounts of "true" components obtained from proper thermodynamic model the compositional dependence of parameters of considered viscosity equations acquires the simple multilinear linear form.

2. Method

The thermodynamic model of Shakhmatkin and Vedishcheva was combined with the commonly used viscosity models (i.e. Adam and Gibbs, Avramov and Milchev, and MYEGA). The compositional dependence of the parameters of considered viscosity models were described by multilinear forms using as independent variables the equilibrium molar amounts of significant components considered in the thermodynamic model.

2.1. Thermodynamic model of Shakhmatkin and Vedishcheva

The model [3,5,6] considers glasses and melts as an ideal solution formed from salt-like products of equilibrium chemical reactions between the simple chemical entities (oxides, halogenides, chalcogenides…) and from the original (un-reacted) entities. These salt-like products (also called associates, groupings, components or species) have the same stoichiometry as the crystalline compounds, which exist in the equilibrium phase diagram of the considered system. The minimization

* Corresponding author.
E-mail address: maria.chromcikova@tnuni.sk (M. Chromčíková).

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Table 1
Glass compositions (mol%), dilatometric glass transition temperature T_g, parameters of VFT equation with standard deviations given in round brackets, standard deviation of approximation, s_{apr}, and Fisher's F-statistics.

Glass	$x(Na_2O)$	$x(MgO)$	$x(CaO)$	$x(SiO_2)$	T_g/K	A (s (A))	B/K (s (B))	T_0/K (s (B))	F	s_{apr}
M0	16.54	0.00	9.92	73.54	819	−1.78 (0.05)	4360 (62)	530 (4)	2208	0.07
M2	16.93	2.68	7.84	72.56	797	−2.11 (0.04)	5003 (56)	481 (3)	3415	0.06
M4	17.39	4.65	5.90	72.06	800	−2.12 (0.08)	5209 (101)	460 (6)	1558	0.08
M6	17.28	5.99	4.13	72.60	792	−2.06 (0.06)	5280 (74)	448 (4)	2623	0.06
M8	17.64	7.05	2.22	73.10	796	−2.08 (0.05)	5438 (71)	437 (4)	2803	0.06
M10	16.66	10.69	0.00	72.65	794	−2.12 (0.02)	5620 (27)	435 (2)	22659	0.02

of the systems Gibbs energy constrained by the overall system composition has to be performed with respect to the molar amount of each system component (species) to reach the equilibrium system composition [14]. The total Gibbs energy is expressed supposing the state of the ideal solution:

$$G\left(n_1, n_2, \ldots n_N\right) = \sum_{i=1}^{N} n_i G_{m,i} + RT \sum_{i=1}^{N} n_i \ln \frac{n_i}{\sum_{j=1}^{N} n_j} \quad (1)$$

where T is the system temperature, N is the number of species, n_i is the molar amount of i-th species and $G_{m,i}$ is the molar Gibbs energy of pure i-th species at the pressure of the system and temperature T. For particular glass at temperature T lower than T_g the $T = T_g$ is used. It means it is supposed that the glass structure is frozen in at T_g.

2.2. Temperature dependence of viscosity

In the following text all the considered viscosity equations are summarized in the final form used for the regression analysis. Only the semi-empirical viscosity models were considered for regression treatment. In all used viscosity equations the η_∞ abbreviates the high temperature viscosity limit and the $\eta(T_g) = 10^{13}$ dPa·s constraint takes place (i.e. the fixed value of 10^{13} dPa·s is used for viscosity at T_g). The details can be found in our previous work [7].

a) Adam and Gibbs configuration entropy equation [8,9] (or AG-equation):

$$\log\eta = \log\eta_\infty + \left\{T\left[\left(T_g(13 - \log\eta_\infty)\right)^{-1} + \left(\Delta c_p/B\right)\ln\left(T/T_g\right)\right]\right\}^{-1} \quad (2)$$

where T_g is the glass transition temperature and Δc_p represents the temperature independent difference between the isobaric molar heat capacity of metastable melt, $c_{p,m}$, and glass, $c_{p,g}$.

b) Avramov and Milchev equation [8,10] (or AM-equation):

$$\log\eta = \log\eta_\infty + (13 - \log\eta_\infty)\left(T_g/T\right)^{\alpha}. \quad (3)$$

c) MYEGA equation [8,11] (or MY-equation):

$$\log\eta = \log\eta_\infty + (13 - \log\eta_\infty)\left(T_g/T\right)\exp\left[(\alpha - 1)\left(\left(T_g/T\right) - 1\right)\right] \quad (4)$$

where the α parameter has the same physical meaning like in the case of Avramov and Milchev viscosity equation.

2.3. Accounting for viscosity compositional dependence

In all viscosity equations considered in the present work the high temperature limit of viscosity value, $\log\eta_\infty$ (frequently abbreviated as A), represents one of the estimated parameters. There were some attempts [8] to treat this value as composition independent. Therefore both cases, i.e. composition-dependent (abbreviated as AV) and composition-independent (abbreviated as AC), are considered in the present work.

Choosing one of the above viscosity equations describing the temperature–viscosity dependence, the viscosity–composition dependence can be introduced by expressing the unknown parameters (e.g. $\log\eta_\infty$, B, Δc_p, and α) as multilinear forms of equilibrium molar amounts, n_i, of system components obtained from the thermodynamic model:

$$\log\eta_\infty = \sum_{i=1}^{4} a_i n_i \quad (5)$$

$$B = \sum_{i=1}^{4} b_i n_i \quad (6)$$

$$\Delta c_p = \sum_{i=1}^{4} c_i n_i \quad (7)$$

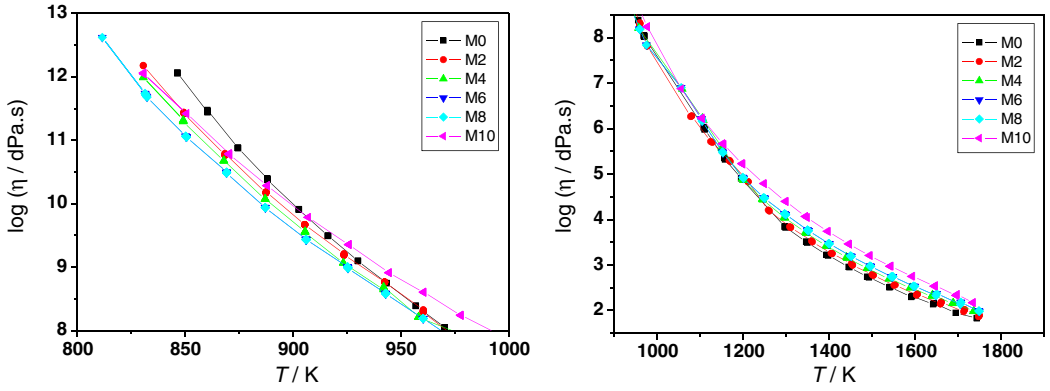

Fig. 1. Experimental viscosity values (the lines are only for eye guidance).