

THERMODYNAMIC MODEL AND VISCOSITY OF SELECTED ZIRCONIA CONTAINING SILICATE GLASSES

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The compositional dependence of viscosity, and viscous flow activation energy of glasses with composition $x\text{Na}_2\text{O} \cdot (15-x)\text{K}_2\text{O} \cdot y\text{CaO} \cdot (10-y)\text{ZnO} \cdot z\text{ZrO}_2 \cdot (75-z)\text{SiO}_2$ ($x = 0, 7.5, 15$; $y = 0, 5, 10$; $z = 0, 1, 3, 5, 7$) was analyzed. The studied glasses were described by the thermodynamic model of Shakhmatkin and Vedishcheva considering the glass as an equilibrium ideal solution of species with stoichiometry given by the composition of stable crystalline phases of respective glass forming system. Viscosity-composition relationships were described by the regression approach considering the viscous flow activation energy and the particular isokome temperature as multilinear function of equilibrium molar amounts of system components. The classical approach where the mole fractions of individual oxides are considered as independent variables was compared with the thermodynamic model. On the basis of statistical analysis there was proved that the thermodynamic model is able to describe the composition property relationships with higher reliability. Moreover, due its better physical justification, thermodynamic model can be even used for predictive purposes.

INTRODUCTION

The physical properties of $x\text{Na}_2\text{O} \cdot (15-x)\text{K}_2\text{O} \cdot y\text{CaO} \cdot (10-y)\text{ZnO} \cdot z\text{ZrO}_2 \cdot (75-z)\text{SiO}_2$ ($x = 0, 7.5, 15$; $y = 0, 5, 10$; $z = 0, 1, 3, 5, 7$) glasses and glass melts were studied in our previous work [1-6]. The reason for this study was the extraordinary importance of this glass system for glass technology, namely for Portland cement composites and for the replacement of toxic oxides (barium oxide, lead oxide) in crystal glass in order to minimize the impact of glass production on the environment, to minimize health hazards of the product, and to increase its dishwashing resistance [7-9]. The knowledge of the property-composition relationships is the compulsory prerequisite for targeted optimization of the glass composition. The standard treatment considering the particular property as a multilinear function of molar fractions of individual oxides often fails and needs an empirical addition of interaction terms represented by products and/or powers of independent variables. Therefore the aim of the present work resides in application of thermodynamic model of Shakhmatkin and Vedishcheva for viscosity-composition multilinear regression where the multilinear form of property - composition relationships (with the composition expressed by the equilibrium molar amounts of systems components) is expected.

EXPERIMENTAL

The glass batches were prepared by mixing of powdered carbonates and oxides. Glasses were melted in Pt - 10 % Rh crucible in superkanthal furnace at temperature of 1600°C for two-three hours in ambient atmosphere. The homogeneity was ensured by repeated hand mixing of the melt. The glass melt was then poured onto a stainless steel plate. The samples were tempered in a muffle furnace for one hour at 650°C, after which the furnace was switched off and samples allowed remain there until completely cool.

The chemical composition of studied glasses was determined after their decomposition by the mixture of HF and HClO₄ by inductively coupled plasma optical emission spectroscopy (VARIAN - Vista MPX / ICP-OES). The content of SiO₂ has not been analyzed. Chemical composition of studied silicate glasses is summarized in Table 1.

The low-temperature viscosities between 10⁸ dPa.s and 10¹² dPa.s were measured by thermomechanical analyzer (Netzsch, TMA 402). The viscosity value, η , was calculated from the measured deformation rate $d\varepsilon/dt$ and the known value of axial load G on orthorhombic (approx. 5 mm × 5 mm × 20 mm) sample with cross-section S :

$$\eta = \frac{G}{3S (d\varepsilon/dt)} \quad (1)$$

The high-temperature viscosity values in the range from $10^{1.8}$ dPa.s to 10^3 dPa.s were measured by the falling ball method [10].

The low- and high-temperature viscosity data were separately described by the Andrade's equation:

$$\log(\eta/\text{dPa}\cdot\text{s}) = A_{\text{low/high}} + \frac{B_{\text{low/high}}}{T} = A_{\text{low/high}} + \frac{2.303E_{\text{low/high}}}{RT} \quad (2)$$

where $E_{\text{low/high}}$ is the low-/high-temperature viscosity activation energy. After that the full range of viscosity data was described by the Vogel Fulcher Tammann equation [11-13]:

$$\log(\eta/\text{dPa}\cdot\text{s}) = A_{\text{VFT}} + \frac{B_{\text{VFT}}}{T - T_0} \quad (3)$$

and the isokome temperatures, T_x , were evaluated according to:

$$T_x = T_0 + \frac{B_{\text{VFT}}}{(x - A_{\text{VFT}})} \quad (4)$$

where $x = (2, 4, 5, 7.65, 13, \text{ and } 14.5)$ dPa.s.

Experimental details can be found in [1-5]. Such obtained experimental data used for presented regression treatment are summarized in Table 2.

THEORETIC

Thermodynamic model

Shakhmatkin and Vedishcheva proposed the thermodynamic model (TD) of glasses and glassforming melts [14-21] that could be considered as the extension of the Conrad's model [22, 23]. This model considers

Table 1. The composition (mol. %) and parameters of VFT Equation (3) of studied glasses [1-3, 5].

Glass	Na ₂ O	K ₂ O	CaO	ZnO	ZrO ₂	SiO ₂	A_{VFT}	B_{VFT} (K)	T_0 (K)
NCZ0	15.30	0	9.22	0	0	75.48	-1.216	3738	545
NCZ1	13.86	0	10.69	0	0.93	74.52	-1.474	4199	545
NCZ3	13.42	0	10.19	0	2.86	73.53	-1.823	4523	559
NCZ5	14.99	0	10.00	0	4.87	70.14	-2.030	4693	584
NCZ7	14.07	0	9.78	0	6.77	69.38	-2.804	5572	566
KCZ0	0	14.98	8.42	0	0	76.60	-1.331	3963	607
KCZ1	0	14.29	8.44	0	1.02	76.25	-1.729	4383	609
KCZ3	0	15.41	10.08	0	3.28	71.23	-2.164	4687	625
KCZ5	0	15.44	10.06	0	4.92	69.58	-2.040	4449	670
NzZ0	14.80	0	0	9.90	0	75.30	-1.548	4641	483
NzZ1	15.04	0	0	9.41	1.03	74.52	-2.096	5196	471
NzZ3	15.29	0	0	11.04	3.19	70.48	-2.413	5490	500
NzZ5	14.77	0	0	9.01	4.90	71.32	-2.432	5592	531
NzZ7	14.18	0	0	9.89	6.54	69.39	-2.699	5747	552
KzZ0	0	15.74	0	8.47	0	75.79	-2.953	6791	438
KzZ1	0	14.93	0	10.49	0.97	73.61	-3.039	6760	477
KzZ3	0	14.20	0	9.86	2.80	73.14	-2.648	6025	574
KzZ5	0	16.00	0	10.44	4.91	68.65	-2.954	6030	613
NKCZ1	7.64	7.36	8.61	0.00	0.95	75.44	-2.002	5478	451
NKzZ1	7.45	7.41	0.00	10.08	0.98	74.08	-2.232	6117	416
NCzZ1	13.51	0.00	4.80	4.58	0.89	76.22	-1.133	4127	525
KCzZ1	0.00	15.81	5.03	5.27	1.01	72.88	-1.523	4415	533
NKCzZ1	8.22	8.01	4.40	5.40	1.05	72.92	-2.239	5662	520
NKCZ3	7.54	7.44	8.84	0	2.86	73.32	-2.271	5796	467
NKzZ3	7.30	7.06	0	9.63	2.61	73.40	-2.049	5523	504
NCzZ3	13.72	0	4.72	5.01	2.71	73.84	-1.967	5070	504
KCzZ3	0	13.95	4.47	4.95	2.66	73.97	-1.578	4473	563
NKCzZ3	6.61	6.96	4.41	4.81	2.58	74.63	-1.776	5008	593
NKCZ5	7.74	6.89	9.97	0	5.12	70.28	-2.153	5074	554
NKzZ5	7.66	7.13	0	10.92	5.22	69.07	-3.090	6705	482
NCzZ5	15.78	0	5.13	5.58	5.42	68.09	-2.714	5577	510
KCzZ5	0	13.64	4.97	5.48	5.20	70.72	-2.954	6312	562
NKCzZ5	7.82	7.18	5.18	5.63	5.35	68.85	-2.711	5957	496
NKCZ7	7.66	7.01	9.98	0	7.18	68.17	-2.373	5056	597
NKzZ7	7.83	7.00	0	11.03	7.54	66.60	-2.679	5772	564
NCzZ7	15.78	0	5.11	5.43	7.40	66.29	-3.134	6086	521
NKCzZ7	7.86	6.99	5.00	5.53	7.40	67.22	-3.785	7499	456

glasses and melts as a solution formed from salt-like products of interaction between the oxide components and from the original (unreacted) oxides. These salt-like products (also called associates, groupings or species) have the same stoichiometry as the crystalline compounds, which exist in the equilibrium phase diagram of the system considered. The model does not use adjustable parameters; only the standard Gibbs energies of formation of crystalline compounds and the analytical composition of the system considered are used as input parameters. On the basis of the crystal structure of stable crystalline phases some information about the glass structure can be reached and compared with experimental results [24, 25].

The minimization 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 to reach the equilibrium system com-

position [26]. The total Gibbs energy is expressed supposing the state of the ideal solution:

$$G(n_1, n_2, \dots, n_N) = \sum_{i=1}^N n_i \Delta_f G_{m,i} + RT \sum_{i=1}^N n_i \ln \left(\frac{n_i}{\sum_{j=1}^N n_j} \right) \quad (5)$$

where N is the number of components, n_i is the molar amount of i -th component, T is the system temperature (i.e. the glass transition temperature, T_g , for particular glass) and $\Delta_f G_{m,i}$ is the molar Gibbs formation energy of pure i -th component at the pressure of the system and temperature T . The system components are ordered such way that X_i ($i = 1, 2, \dots, M < N$) are pure oxides and X_i ($i = M + 1, M + 2, \dots, N$) are compounds formed from oxides by reversible reactions

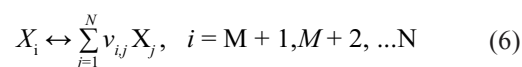


Table 2. The isokome temperatures and viscous flow activation energies.

Glass	E_{low} (kJ.mol ⁻¹)	E_{high} (kJ.mol ⁻¹)	T_2 (K)	T_4 (K)	T_5 (K)	$T_{7.65}$ (K)	T_{13} (K)	$T_{14.5}$ (K)
NCZ0	489	196	1707	1262	1146	967	808	783
NCZ1	489	195	1753	1312	1193	1005	835	808
NCZ3	510	204	1742	1336	1222	1037	864	836
NCZ5	539	216	1735	1353	1244	1063	893	865
NCZ7	571	244	1726	1385	1280	1099	919	888
KCZ0	561	208	1797	1351	1233	1049	884	858
KCZ1	570	210	1785	1374	1261	1077	907	879
KCZ3	632	242	1750	1385	1279	1102	934	906
KCZ5	726	298	1771	1407	1302	1129	966	939
NzZ0	423	202	1791	1319	1192	992	802	775
NzZ1	426	227	1740	1324	1204	1005	816	785
NzZ3	461	230	1744	1357	1241	1046	857	825
NzZ5	504	254	1792	1400	1283	1085	893	861
NzZ7	529	259	1775	1410	1298	1107	918	886
KzZ0	429	242	1809	1415	1292	1079	864	827
KzZ1	463	259	1818	1437	1318	1110	899	863
KzZ3	579	281	1870	1480	1362	1159	959	925
KzZ5	689	312	1830	1480	1371	1182	991	958
NKCZ1	472	214	1787	1333	1210	1015	837	809
NKzZ1	385	223	1861	1397	1261	1035	817	781
NCzZ1	466	208	1842	1329	1198	995	817	789
KCzZ1	478	237	1855	1427	1302	1092	891	858
NKCzZ1	408	220	1819	1363	1233	1018	816	783
NKCZ3	522	235	1813	1365	1243	1048	870	841
NKzZ3	462	240	1867	1418	1289	1074	871	837
NCzZ3	465	228	1782	1353	1231	1031	842	812
KCzZ3	552	249	1919	1460	1332	1124	932	900
NKCzZ3	422	211	1824	1391	1264	1051	847	813
NKCZ5	509	239	1776	1379	1264	1072	889	859
NKzZ5	473	255	1800	1428	1311	1106	899	863
NCzZ5	508	251	1692	1340	1233	1048	865	834
KCzZ5	644	351	1837	1470	1356	1158	958	924
NKCzZ5	471	246	1760	1383	1268	1070	875	842
NKCZ7	582	250	1753	1390	1282	1101	926	896
NKzZ7	574	278	1798	1428	1316	1123	932	900
NCzZ7	515	253	1705	1374	1269	1085	898	866
NKCzZ7	509	300	1754	1413	1304	1109	908	874

Let us suppose the system composition given by the molar amounts of pure unreacted oxides $n_{0,j}$ ($j = 1, 2, \dots, M$). Then the mass balance constraints can be written in the form:

$$n_{0,j} = n_j + \sum_{i=M+1}^N v_{ij} X_i, \quad j = 1, 2, \dots, N \quad (7)$$

The molar Gibbs formation energies of the melts of pure components may be used in more advanced version of this model. However these thermodynamic data are relatively scarce that prevents routine application of the model to the study of multicomponent systems. On the other hand the errors caused by substituting the melt by the crystalline state are partially compensated when the reaction Gibbs energy, $\Delta_r G_{m,i}$ is calculated according:

$$\Delta_r G_{m,i} = \Delta_f G_{m,i} - \sum_{j=1}^N v_{ij} \Delta_f G_{m,j} = -RT \ln K_i, \quad (8)$$

$$i = M+1, M+2, \dots, N$$

where K_i is the equilibrium constant of the i -th equilibrium reaction described by the Equation 6.

When the crystalline state data are used the model can be simply applied to most multicomponent glasses including the non-oxide ones. Especially the application of the model to the multicomponent industrially produced glasses can be very important. Taking into account that the common praxis resides in expressing most of the multicomponent glass properties in the form of (mostly) additive functions of the glass composition expressed in percents (even weight and not molar!) of pure oxides [27–29] using the thermodynamic model unambiguously represents the significant progress.

The contemporary databases of thermodynamic properties (like the FACT computer database [30]) enable the routine construction of the Shakhmatkin and Vedishcheva model [21] for most of important multicomponent systems. It is worth noting that other methods of thermodynamic modeling of glasses and glassforming melts (not discussed here, e.g. [31, 32, 33]) do not possess the possibility of routine application to multicomponent systems.

RESULTS AND DISCUSSION

The 26 stable crystalline phases considered in the studied glass system are summarized in Table 3. For each glass composition the TD model was evaluated at the glass transition temperature. The system was created from one mole of individual oxides, i.e.:

$$n_0(\text{Na}_2\text{O}) + n_0(\text{K}_2\text{O}) + n_0(\text{CaO}) + n_0(\text{ZnO}) + n_0(\text{ZrO}_2) + n_0(\text{SiO}_2) = 1 \text{ mol} \quad (9)$$

Thirteen species with significant equilibrium abundance were found (see Table 3 where these components are numbered). Threshold of 0.01 mol of oxides was applied for qualification of significant species abundance. Equilibrium molar amounts of these species are

summarized in Table 4. With the exception of SiO_2 the dependence of equilibrium molar amounts of significant components on $n_0(\text{ZrO}_2)$ given by the glass chemical analysis is plotted in Figure 1.

The isokome temperatures, T_x , were calculated for each glass composition from the VFT parameters summarized in Table 1 for viscosity values of $\log(h(T_x/\text{dPa.s})) = x = 2, 4, 5, 7.65, 13$, and 14.5.

The property compositional dependences of isokome temperatures were described by the multilinear equation:

$$T_x = a_0^x + \sum_{i=1}^{13} a_i^x n_i \quad (10)$$

analogously were described the compositional dependences of the low- and high-temperature viscous flow activation energy.

Multilinear regression analysis was used for obtaining of estimates of the a_i parameters together with their standard deviations. By starting from the full equation (10) the statistically non-significant terms were rejected

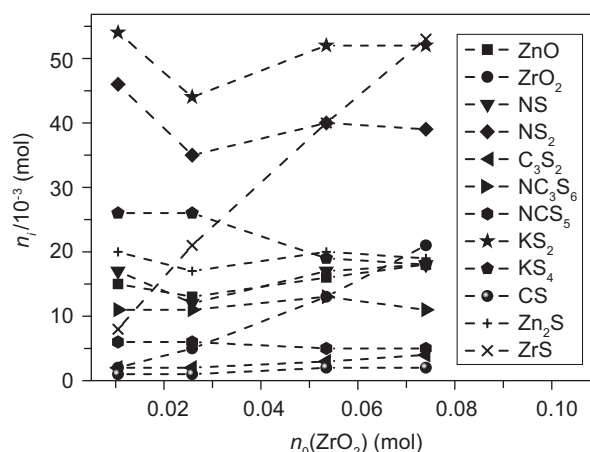


Figure 1. Equilibrium molar amounts of individual components (with the exception of SiO_2) in NKCzZx ($x = 1, 3, 5, 7$) glasses (data taken from Table 4).

Table 3. Stable crystalline phases considered in the Na_2O – K_2O – CaO – ZnO – ZrO_2 – SiO_2 system [34]. Components with significant abundance in studied glasses are numbered.

Stoichiometry	No.	Abbrev.	Stoichiometry	No.	Abbrev.
Na_2O	-	Na2O	$\text{Na}_2\text{Ca}_3\text{Si}_6\text{O}_{16}$	7	NC3S6
K_2O	-	K2O	$\text{Na}_2\text{CaSi}_5\text{O}_{12}$	8	NCS5
CaO	-	CaO	K_2SiO_3	-	KS
ZnO	1	ZnO	K_2SiO_4	9	KS2
ZrO_2	2	ZrO2	$\text{K}_2\text{Si}_4\text{O}_9$	10	KS4
SiO_2	3	SiO2	CaSiO_3	11	CS
Na_2SiO_3	4	NS	Ca_2SiO_4	-	C2S
$\text{Na}_2\text{Si}_2\text{O}_5$	5	NS2	Ca_3SiO_5	-	C3S
Na_4SiO_4	-	N2S	$\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_9$	-	NC2S3
$\text{Na}_4\text{CaSi}_3\text{O}_9$	-	N2CS3	$\text{Ca}_2\text{ZnSi}_2\text{O}_7$	-	C2ZnS2
$\text{Na}_6\text{Si}_2\text{O}_5$	-	N3S2	CaZrO_3	-	CZr
$\text{Na}_6\text{Si}_8\text{O}_{19}$	-	N3S8	Zn_2SiO_4	12	Zn2S
$\text{Ca}_3\text{Si}_2\text{O}_7$	6	C3S2	ZrSiO_4	13	ZrS

in a stepwise manner. The statistical significance of a_i ($i = 0, 1, \dots, 13$) estimates was determined on the basis of the Student's t -statistics at 95 % significance level. The overall statistical quality of regression equation was characterized by standard deviation of approximation s_{appr} . The obtained results are summarized in Tables 5 and 6.

For comparison, the analogous multilinear regression treatment of experimental data was applied by using the molar amounts of individual oxides (constrained by the Equation 9 and hence numerically equal to mole fractions) as independent variables:

$$T_x = a_0^x + \sum_{i=1}^{13} a_i^x n_i \quad (11)$$

analogously were described the compositional dependences of the low- and high-temperature viscous flow activation energy.

This “*pure oxides model*” represents the common way of property-composition dependence description used in the glass science and technology [29]. The obtained results are summarized, together with the results of the thermodynamic model, in Tables 5 and 6.

Comparing the regression results obtained by both models one can see that the values of standard deviation of approximation, s_{appr} , are significantly lower for the thermodynamic model than for the pure oxides model with the exception of T_2 and T_4 isokome temperature where both regression treatments resulted in practically the same value of s_{appr} . The same picture is obtained when the correlation coefficients, r , are compared (i.e. lower s_{appr} value is connected with the r value closer to one). This situation can be explained by the fact that the equilibrium molar amounts of individual components of the thermodynamic mode are calculated at T_g tempe-

Table 4. Equilibrium molar amounts n_i (given in 10^{-3} mol) of species with significant abundance in studied glasses. Species numbering is given in Table 3.

Glass	n_1	n_2	n_3	n_4	n_5	n_6	n_7	n_8	n_9	n_{10}	n_{11}	n_{12}	n_{13}
NCZ0	0	0	336	27	85	3	24	13	0	0	1	0	0
NCZ1	0	2	323	22	70	4	28	14	0	0	1	0	8
NCZ3	0	6	314	22	67	4	26	14	0	0	2	0	23
NCZ5	0	12	251	29	76	6	24	13	0	0	2	0	37
NCZ7	0	18	251	27	68	8	21	14	0	0	3	0	49
KCZ0	0	0	286	0	0	0	0	0	101	48	84	0	0
KCZ1	0	3	290	0	0	0	0	0	95	48	84	0	8
KCZ3	0	10	210	0	0	0	0	0	118	36	100	0	23
KCZ5	0	18	189	0	0	0	0	0	120	34	100	0	31
NzZ0	19	0	452	36	111	0	0	0	0	0	0	40	0
NzZ1	20	2	435	37	112	0	0	0	0	0	0	37	8
NzZ3	24	7	370	41	111	0	0	0	0	0	0	43	25
NzZ5	22	11	383	39	108	0	0	0	0	0	0	34	38
NzZ7	25	15	361	39	102	0	0	0	0	0	0	37	50
KzZ0	20	0	301	0	0	0	0	0	102	55	0	32	0
KzZ1	25	2	287	0	0	0	0	0	97	52	0	40	7
KzZ3	28	8	288	0	0	0	0	0	89	52	0	35	20
KzZ5	33	18	212	0	0	0	0	0	115	44	0	36	31
NKCZ1	0	2	281	11	32	3	24	7	46	28	1	0	8
NKzZ1	21	2	362	19	55	0	0	0	47	27	0	40	8
NCzZ1	12	1	416	27	85	2	11	10	0	0	1	17	7
KCzZ1	16	3	249	0	0	0	0	0	113	44	50	18	7
NKCzZ1	15	2	278	17	46	2	11	6	54	26	1	20	8
NKCZ3	0	6	250	11	30	4	24	7	49	25	2	0	22
NKzZ3	22	5	357	19	54	0	0	0	45	25	0	37	21
NCzZ3	14	5	375	28	85	2	10	11	0	0	1	18	22
KCzZ3	16	7	290	0	0	0	0	0	94	45	44	17	20
NKCzZ3	13	5	332	12	35	2	11	6	44	26	1	17	21
NKCZ5	0	14	210	11	27	6	26	6	48	21	3	0	38
NKzZ5	26	13	293	22	54	0	0	0	49	22	0	41	39
NCzZ5	17	13	267	39	93	4	11	9	0	0	1	20	41
KCzZ5	21	17	251	0	0	0	0	0	95	41	49	17	35
NKCzZ5	16	13	236	17	40	3	13	5	52	19	2	20	40
NKCZ7	0	22	187	12	26	8	24	6	51	19	4	0	50
NKzZ7	30	23	262	24	54	0	0	0	50	19	0	40	53
NCzZ7	18	21	244	41	91	5	10	9	0	0	2	18	53
NKCzZ7	18	21	220	18	39	4	11	5	52	18	2	19	53

Table 5. Results of multilinear regression analysis (Equations (10) and (11)), s_{apr} - standard deviation of approximation, r - correlation coefficient.

Comp.	Value	E_{low} (kJ.mol ⁻¹)	E_{high} (kJ.mol ⁻¹)	T_2 (K)	T_4 (K)
	a_0	—	—	2389 ± 154	1202 ± 48
ZnO	a_1	—	3316 ± 746	—	—
ZrO ₂	a_2	15487 ± 857	5214 ± 597	-4228 ± 1134	—
SiO ₂	a_3	—	—	—	—
NS	a_4	-17154 ± 2664	-5904 ± 1276	-5382 ± 1373	-8372 ± 1834
NS ₂	a_5	9283 ± 933	3241 ± 496	—	3305 ± 987
C ₃ S ₂	a_6	-11926 ± 5050	—	—	—
NC ₃ S ₆	a_7	3950 ± 1248	3423 ± 572	-5462 ± 1559	—
NCS ₅	a_8	8301 ± 2028	—	-6503 ± 2838	2198 ± 932
KS ₂	a_9	—	—	-2127 ± 813	—
KS ₄	a_{10}	7976 ± 226	2890 ± 350	-5748 ± 2232	3316 ± 1021
CS	a_{11}	1820 ± 172	901 ± 191	-1080 ± 321	—
Zn ₂ S	a_{12}	—	—	—	1305 ± 312
ZrS	a_{13}	—	—	—	2880 ± 380
	s_{apr}	26	13	31	14
	r	0.999	0.999	0.843	0.968
	b_0	481 ± 20	222 ± 7	2228 ± 103	1575 ± 53
Na ₂ O	b_1	-662 ± 142	-305 ± 50	-2934 ± 699	-1637 ± 361
K ₂ O	b_2	615 ± 208	—	-2427 ± 683	-1012 ± 353
CaO	b_3	—	—	-550 ± 123	-555 ± 64
ZnO	b_4	—	242 ± 70	—	—
ZrO ₂	b_5	1699 ± 355	965 ± 125	-425 ± 208	1066 ± 108
	s_{apr}	51	18	30	15
	r	0.769	0.865	0.832	0.955

Table 6. Results of multilinear regression analysis (Equations (10) and (11)), s_{apr} - standard deviation of approximation, r - correlation coefficient.

Comp.	Value	T_5 (K)	$T_{7.65}$ (K)	T_{13} (K)	$T_{14.5}$ (K)
	a_0	1025 ± 44	820 ± 51	—	—
ZnO	a_1	—	—	—	—
ZrO ₂	a_2	—	—	3940 ± 1658	4385 ± 1728
SiO ₂	a_3	—	—	—	—
NS	a_4	-8852 ± 1561	-9140 ± 1811	-17657 ± 1648	-17425 ± 1717
NS ₂	a_5	3707 ± 845	3931 ± 980	11510 ± 706	11274 ± 736
C ₃ S ₂	a_6	—	—	—	—
NC ₃ S ₆	a_7	—	—	7420 ± 1146	7204 ± 1194
NCS ₅	a_8	4650 ± 1162	4774 ± 1348	11125 ± 1181	10575 ± 1230
KS ₂	a_9	—	—	1139 ± 435	1046 ± 453
KS ₄	a_{10}	3882 ± 878	3906 ± 1019	11445 ± 662	11124 ± 690
CS	a_{11}	421 ± 128	594 ± 149	2512 ± 407	2477 ± 424
Zn ₂ S	a_{12}	1757 ± 335	1366 ± 389	3697 ± 957	3446 ± 997
ZrS	a_{13}	3395 ± 327	3710 ± 380	4367 ± 704	4056 ± 734
	s_{apr}	11	13	15	16
	r	0.979	0.971	1.000	1.000
	b_0	1372 ± 51	1059 ± 6	880 ± 7	848 ± 7
Na ₂ O	b_1	-1432 ± 350	-597 ± 46	-541 ± 58	-525 ± 62
K ₂ O	b_2	-797 ± 343	—	—	—
CaO	b_3	—	—	—	—
ZnO	b_4	462 ± 59	261 ± 65	—	—
ZrO ₂	b_5	1223 ± 104	1423 ± 116	1427 ± 146	1393 ± 154
	s_{apr}	15	17	21	22
	r	0.960	0.947	0.906	0.891

perature, and the T_2 and T_4 temperatures are the most distant from the glass transition temperature. For the case of the low temperature viscosity activation energy and T_{13} isokome temperature the graphical comparison of both fits is presented in Figures 2 and 3.

For practical use of the above treatment for an arbitrary glass composition the compositional dependence of glass transition temperature is needed. This was published in our previous work [6]:

$$T_g/K = 6637 n(\text{ZrO}_2) - 1576 n(\text{NS}) + 10596 n(\text{NS2}) + 4467 n(\text{C3S2}) + 7884 n(\text{NC3S6}) + 11529 n(\text{NCS5}) + 932 n(\text{KS2}) + 11217 n(\text{KS4}) + 2642 n(\text{CS}) + 4613 n(\text{Zn2S}) + 2255 n(\text{ZrS})$$

However some iterative scheme of solving the above equation is needed, i.e. the TD model has to be solved for the temperature sufficiently close to the T_g value obtained from the result of TD model solution.

As a zero approximation of T_g value can be used the value predicted by the pure oxide model [6]:

$$T_g/K = 866 - 503 n_0(\text{Na}_2\text{O}) + 1204 n_0(\text{ZrO}_2)$$

It is worth noting, that after calculation of isokome temperatures according to Equation 10 by using the data of Tables 5 and 6 the detailed temperature dependence of viscosity can be obtained e.g. by regression analysis of isokome temperatures using the VFT Equation 3.

CONCLUSIONS

The thermodynamic model of studied Na_2O – K_2O – CaO – ZnO – ZrO_2 – SiO_2 glasses revealed 13 components with significant equilibrium abundance at the T_g temperature. The compositional dependence of viscous flow activation energy and isokome temperatures was

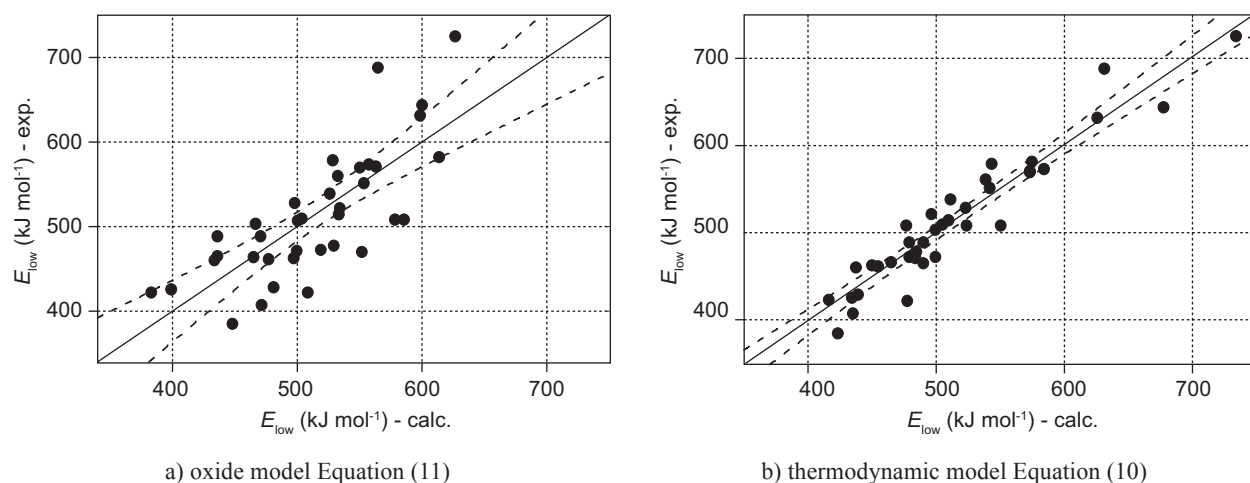


Figure 2. Comparison of experimental and calculated values of low-temperature activation energy of viscous flow: a) oxide model Equation (11); b) thermodynamic model Equation (10). Dotted lines represent the 95 % confidence limit.

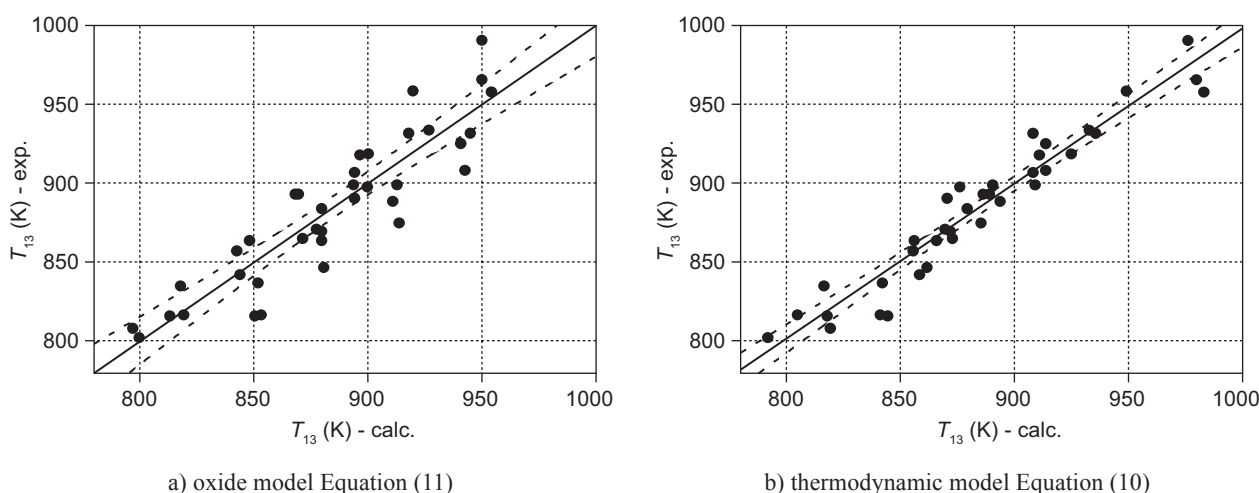


Figure 3. Comparison of experimental and calculated values of T_{13} isokome temperature: a) oxide model Equation (11); b) thermodynamic model Equation (10). Dotted lines represent the 95-% confidence limit.

successfully described in frame of the Shakhmatkin and Vedishcheva thermodynamic model by multilinear regression function of equilibrium molar amounts of significant components. The present treatment of the composition-temperature dependence of glass viscosity enables the prediction of viscosity-temperature dependence for arbitrary glass composition including those that are outside the studied compositional range.

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