

CONFIGURATIONAL ENTROPY OF SELECTED ZIRCONIA CONTAINING SILICATE GLASSES

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The parameters of Adam-Gibbs equation (AG) were estimated for 28 glasses from the 15(K₂O, Na₂O)·10(ZnO, CaO)·75(ZrO₂, SiO₂) system. Configurational entropy at glass transition temperature, $S^{\text{conf}}(T_g)$, and the B_{AG} parameter of AG equation were expressed as linear functions of the glass composition given in molar fractions of oxides. The same value of the A_{AG} parameter was used for all studied systems. The resulting AG equation described the experimental viscosity values with acceptable accuracy in the high temperature region. The obtained compositional trend of $S^{\text{conf}}(T_g)$ corresponds well with the structural function of particular oxides.

INTRODUCTION

The viscosity temperature dependence of glass forming melts is within the range of more than ten orders well described by the empirical Vogel-Fulcher-Tammann (VFT) equation [1-3]:

$$\log \eta = A_{\text{VFT}} + \frac{B_{\text{VFT}}}{T - T_0} \quad (1)$$

where A_{VFT} , B_{VFT} and T_0 are adjustable parameters.

An alternative non-empirical approach based on the theory of configuration entropy results in the Adam – Gibbs (AG) equation that describes the viscosity temperature dependence with comparable accuracy [4]:

$$\log \eta = A_{AG} + \frac{B_{AG}}{TS^{\text{conf}}(T)} \quad (2)$$

where A_{AG} and B_{AG} are adjustable parameters and S^{conf} is the molar configurational entropy at thermodynamic temperature T . The configurational entropy can be expressed as:

$$S^{\text{conf}}(T) = S^{\text{conf}}(T_g) + \int_{T_g}^T \frac{\Delta C_p^{\text{conf}}}{T} c T \quad (3)$$

The configurational isobaric heat capacity ΔC_p^{conf} is defined as the difference between the heat capacity of the melt, $C_{p,l}$, and that of the glass, $C_{p,g}$, at the glass transition temperature T_g :

$$\Delta C_p^{\text{conf}} = C_{p,l} - C_{p,g}(T_g) \quad (4)$$

The configurational heat capacity symbolizes the energy

barrier for changing the structure. According to works [5-7] the glass molar heat capacity below T_g is given by the vibrational contribution only. Therefore $C_{p,g}$ can be considered as constant and approximately equals to $3R = 24.94 \text{ J/molK}$ (R is the molar gas constant).

Various empirical formulas were proposed for the temperature and compositional dependence of the heat capacity of the silicate melts [5-8]. Bouhifd et al. [9] propose the simple additive scheme for the temperature independent melt heat capacity:

$$C_{p,l} = \sum_i C_{p,i} x_i \quad (5)$$

where x_i is the molar fraction and $C_{p,i}$ the molar heat capacity of i -th oxide in the melt.

Under the above assumptions the Adam – Gibbs equation acquires the simple form:

$$\log \eta = A_{AG} + \frac{B_{AG}}{TS^{\text{conf}}(T_g) + T(C_{p,l} - 3R) \ln(T/T_g)} \quad (6)$$

Thus estimates of the unknown values of A_{AG} , B_{AG} and $S^{\text{conf}}(T_g)$ can be obtained by the non linear regression of the experimental viscosity values using the experimental value of T_g . This procedure can be applied independently for each melt composition.

EXPERIMENTAL

The composition of studied glasses was derived from the basic trisilicate glass composition $15\text{Na}_2\text{O} \cdot 10\text{CaO} \cdot 75\text{SiO}_2$ by three equimolar substitutions, namely $\text{K}_2\text{O}/\text{Na}_2\text{O}$, ZnO/CaO , and $\text{ZrO}_2/\text{SiO}_2$. The effect of noticed equimolar substitutions in sodium- and

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potassium-trisilicate glasses $15\text{M}_2\text{O}\cdot 10\text{CaO}\cdot x\text{ZrO}_2\cdot (75-x)\text{SiO}_2$ and $15\text{M}_2\text{O}\cdot 10\text{ZnO}\cdot x\text{ZrO}_2\cdot (75-x)\text{SiO}_2$ ($\text{M} = \text{Na}, \text{K}, x = 1, 3, 5, \text{ and } 7$) was studied in our previous works [10-12].

The glass batches were prepared by mixing of analytical grade purity powdered Na_2CO_3 (AFT), K_2CO_3 (Fluka), ZnO (Fluka), ZrSiO_4 (Aldrich) and SiO_2 (AFT, min. 96.5 %). Sodium sulphate (AFT) and potassium sulphate (Lachema) were used as fining agents.

Glasses were melted in Pt-10%Rh crucible in superkanthal furnace at temperature of 1550°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 remain there until completely cool.

The chemical composition of glasses was determined by optical emission spectroscopy (ICP) after grained glass samples were dissolved in hydrofluoric acid and perchloric acid. The content of SiO_2 has not been analysed. Obtained chemical composition and abbreviation of glass samples is summarized in Table 1.

The low-temperature viscosities between 10^8 and 10^{12} dPas were measured by thermo-mechanical 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. $5 \times 5 \times 20$) mm^3 sample with the cross-section S :

$$\eta = \frac{G}{3S(d\varepsilon/dt)} \quad (7)$$

The high-temperature viscosity values in the range from $10^{1.8}$ dPas to 1000 dPas were measured by the falling ball method [13].

RESULTS AND DISCUSSION

The configurational heat capacity was calculated

Table 1. The abbreviation and analytical composition of glasses in molar %.

Glass	Na ₂ O	K ₂ O	CaO	ZnO	ZrO ₂	SiO ₂	Glass	Na ₂ O	K ₂ O	CaO	ZnO	ZrO ₂	SiO ₂
NCZ0	15.30	-	9.22	-	-	75.48	KCZ0	-	14.98	8.42	-	-	76.60
NCZ1	13.86	-	10.69	-	0.93	74.52	KCZ1	-	14.29	8.44	-	1.02	76.25
NCZ3	13.42	-	10.19	-	2.86	73.53	KCZ3	-	15.41	10.08	-	3.28	71.23
NCZ5	14.99	-	10.00	-	4.87	70.14	KCZ5	-	15.44	10.06	-	4.92	69.58
NCZ7	14.07	-	9.78	-	6.77	69.38							
NzZ0	14.80	-	-	9.90	-	75.30	KzZ0	-	15.74	-	8.47	-	75.79
NzZ1	15.04	-	-	9.41	1.03	74.52	KzZ1	-	14.93	-	10.49	0.97	73.61
NzZ3	15.29	-	-	11.04	3.19	70.48	KzZ3	-	14.20	-	9.86	2.80	73.14
NzZ5	14.77	-	-	9.01	4.90	71.32	KzZ5	-	16.00	-	10.44	4.91	68.65
NzZ7	14.18	-	-	9.89	6.54	69.39							
NKCZ1	7.64	7.36	8.61	-	0.95	75.44	NKCZ3	7.54	7.44	8.84	-	2.86	73.32
NKzZ1	7.45	7.41	-	10.08	0.98	74.08	NKzZ3	7.30	7.06	-	9.63	2.61	73.40
NCzZ1	13.51	-	4.80	4.58	0.89	76.22	NCzZ3	13.72	-	4.72	5.01	2.71	73.84
KCzZ1	-	15.81	5.03	5.27	1.01	72.88	KCzZ3	-	13.95	4.47	4.95	2.66	73.97
NKCzZ1	8.22	8.01	4.40	5.40	1.05	72.92	NKCzZ3	6.61	6.96	4.41	4.81	2.58	74.63

Table 2. Molar heat capacities of oxides in melt state in temperature interval $800 - 1500^\circ\text{C}$.

Oxide	Na ₂ O	K ₂ O	CaO	ZnO	ZrO ₂	SiO ₂
C_p (J/Kmol)	116.46	104.84	58.883	84.471	54.581	77.268

from the heat capacities of pure oxide melts reported in Table 2 [14].

The multilinear regression analysis of experimental viscosity data was performed using the linearised form of the Equation (6):

$$\frac{1}{\log \eta - A_{AG}} = \alpha_{\text{lin}} T + \beta_{\text{lin}} T \ln(T/T_g) \quad (8)$$

$$\text{where } \alpha_{\text{lin}} = \frac{S^{\text{conf}}(T_g)}{B_{AG}} \quad \text{and} \quad \beta_{\text{lin}} = \frac{\Delta C_p^{\text{conf}}}{B_{AG}} \quad (9)$$

The value of A_{AG} was substituted by the A_{VFT} value obtained by nonlinear regression of viscosity data based on the VFT equation (Table 3). The average values of $S^{\text{conf}}(T_g)$ and B_{AG} were then calculated. The purpose of this step was to obtain the reliable starting estimates of $S^{\text{conf}}(T_g)$ and B_{AG} for the nonlinear regression analysis of experimental data based on the Equation (6) that was performed for all samples in the next step. Such way the $S^{\text{conf}}(T_g)$ and B_{AG} estimates were obtained for each glass composition. After that these parameters were approximated by the linear additive model:

$$y = y_0 + y(\text{Na}_2\text{O})x(\text{Na}_2\text{O}) + y(\text{K}_2\text{O})x(\text{K}_2\text{O}) + y(\text{CaO})x(\text{CaO}) + y(\text{ZnO})x(\text{ZnO}) + y(\text{ZrO}_2)x(\text{ZrO}_2) \quad (10)$$

where $y \equiv B_{AG}, S^{\text{conf}}(T_g)$.

The obtained values of y_i were used as starting estimates for the nonlinear regression of full set of viscosity data based on the AG equation reflecting the linear model (10):

$$\log \eta = A_{AG} + \frac{B_{AG,0} + \sum_{i=1}^5 B_{AG,i} x_i}{T[S_0^{\text{conf}} + \sum_{i=1}^5 S_i^{\text{conf}}(T_g) x_i] + \Delta C_p^{\text{conf}} T \ln(T/T_g)} \quad (11)$$

Table 3. Parameters of the VFT equation (1) of studied glasses (s – standard deviation).

Glass	A	$s(A)$	B (K)	$s(B)$ (K)	T_0 (K)	$s(T_0)$ (K)	Glass	A	$s(A)$	B (K)	$s(B)$ (K)	T_0 (K)	$s(T_0)$ (K)
NCZ0	-1.216	0.096	3738	123	545	8	KCZ0	-1.331	0.064	3963	83	607	5
NCZ1	-1.474	0.049	4199	62	545	4	KCZ1	-1.729	0.033	4383	42	609	3
NCZ3	-1.823	0.045	4523	59	559	4	KCZ3	-2.164	0.066	4687	89	625	5
NCZ5	-2.030	0.026	4693	34	584	2	KCZ5	-2.040	0.130	4449	175	670	10
NCZ7	-2.804	0.083	5572	121	566	7	KzZ0	-2.953	0.082	6791	138	438	7
NzZ0	-1.548	0.075	4641	110	483	7	KzZ1	-3.039	0.168	6760	278	477	15
NzZ1	-2.096	0.078	5196	1134	471	7	KzZ3	-2.648	0.126	6025	201	574	11
NzZ3	-2.413	0.040	5490	62	500	4	KzZ5	-2.954	0.218	6030	613	613	18
NzZ5	-2.432	0.092	5592	142	531	8	NKCZ3	-2.271	0.090	5796	142	467	8
NzZ7	-2.699	0.056	5747	84	552	5	NKzZ3	-2.049	0.077	5523	118	504	7
NKCZ1	-2.002	0.086	5478	133	451	8	NCzZ3	-1.967	0.095	5070	138	504	8
NKzZ1	-2.232	0.105	6117	174	416	10	KCzZ3	-1.578	0.103	4473	140	563	9
NCzZ1	-1.133	0.124	4127	172	525	11	NKCzZ3	-1.776	0.070	5008	100	593	6
KCzZ1	-1.523	0.093	4415	130	533	8							
NKCzZ1	-2.239	0.085	5662	131	520	8							

 Table 4. Parameters of Equations (10) and (11) (s – standard deviations).

Parameter	$B_{AG}(i)$ (kJ/mol)	$s[B_{AG}(i)]$ (kJ/mol)	Parameter	$S^{\text{conf}}(T_g)(i)$ (J/molK)	$s[S^{\text{conf}}(T_g)(i)]$ (J/molK)
$B_{AG,0}$	710.3	59.8	$S_0^{\text{conf}}(T_g)$	39.09	4.74
$B_{AG}(\text{Na}_2\text{O})^*$	-	-	$S^{\text{conf}}(T_g)(\text{Na}_2\text{O})$	131.6	14.05
$B_{AG}(\text{K}_2\text{O})$	-320.6	130.1	$S^{\text{conf}}(T_g)(\text{K}_2\text{O})$	62.82	16.30
$B_{AG}(\text{CaO})^*$	-	-	$S^{\text{conf}}(T_g)(\text{CaO})$	41.02	14.98
$B_{AG}(\text{ZnO})$	831.6	181.1	$S^{\text{conf}}(T_g)(\text{ZnO})$	93.00	21.38
$B_{AG}(\text{ZrO}_2)$	-2126	484	$S^{\text{conf}}(T_g)(\text{ZrO}_2)$	-316.3	45.2
			$A_{AG} = -2.030 \pm 0.159$		
$s_{\text{apr}}(\log[\eta/\text{dPas}]) = 0.285$				$F = 28199$	

*statistically non-significant parameter

The results of the nonlinear regression are summarized in Table 4. The same value of the A_{AG} parameter was used for all studied systems [15]. The comparison between experimental and calculated viscosity values is presented in Figure 1. It can be seen that the low viscosity values are reproduced with quite well accuracy. The significant discrepancy between the measured and calculated values can be found for the highest viscosity values where relatively high experimental error can be expected. With respect to this fact the value of the standard deviation of approximation $s(\log(\eta/\text{dPas})) = 0.285$ seems acceptable.

The values of the y_i coefficients in Table 4 correspond to the effect of equimolar substitution of SiO_2 by the i -th oxide. It can be seen that the modifying oxides increase the value of configurational entropy in harmony with the assumption of their disordering influence on the glass structure.

The networkforming activity of ZrO_2 that heals the depolymerised silicate network by its six-coordination manifests itself by extremely negative value -316 J/molK. The effect of individual oxides on the B_{AG} value is unclear. This is caused by the statistical insignificance of $B(\text{Na}_2\text{O})$ and $B(\text{CaO})$ parameters.

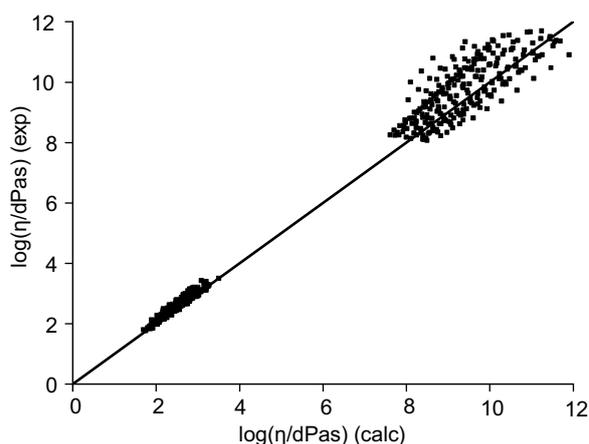


Figure 1. Comparison of experimental (exp) and calculated (calc) values of viscosity.

CONCLUSIONS

The parameters of Adam - Gibbs equation (AG) at glass transition temperature were expressed as linear functions of the glass composition given in

molar fractions of oxides for 28 glasses from the $15(\text{K}_2\text{O}, \text{Na}_2\text{O}) \cdot 10(\text{ZnO}, \text{CaO}) \cdot 75(\text{ZrO}_2, \text{SiO}_2)$ system. Only one A_{AG} parameter was estimated for all studied glasses. The obtained compositional trend of $S^{\text{conf}}(T_g)$ corresponds well with the structural function of particular oxides.

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