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Identification of surface active components in glass forming melts by thermodynamic model



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ABSTRACT

Nine compositional series of $15(\text{Na}_2\text{O}, \text{K}_2\text{O}) \cdot 10(\text{CaO}, \text{ZnO}) \cdot 75(\text{ZrO}_2, \text{SiO}_2)$ glass-forming melts were studied, all with the ZrO_2 content of 0, 1, 3, 5 and 7 mol.%. The investigated glass compositions were obtained by equimolar substitutions $\text{ZrO}_2 / \text{SiO}_2$, ZnO / CaO and $\text{K}_2\text{O} / \text{Na}_2\text{O}$. Surface tension of studied glassforming melts was determined by the sessile and pendant drop profile numerical analysis in the temperature range (1250 - 1500) °C. The experimental values of melt density were used. The linear temperature dependence of surface tension was observed for all samples with only small differences between values obtained from sessile and pendant drop profiles. The Shakhmatkin and Vedishcheva thermodynamic model (TDM) was evaluated for each glass melt at temperature of 1400 °C. The total number of 36 components was considered in TDM. Only 26 components were present with non-negligible equilibrium amount. The surface tension was described by the multilinear function of equilibrium amounts of statistically independent non-negligible components of the TDM. The surface active components were identified by negative values of their coefficients. Such way the N3S8 and C2ZrS4 were identified as “strongly” surface active and NCS5 and KS4 as probably surface active. Regarding the oxide compositional point of view, the surface tension was mostly influenced by ZnO (increase with the addition of the oxide) and by K_2O (decrease with the addition of the oxide).

Introduction

The influence of surface tension accompanies the process of glass production from the glass melting, through the refinement, to the shaping of the product [1]. Moreover the glass resistance against weathering and corrosion (e.g. in dishwashing machines) depends on the glass composition and properties of its surface [2–8]. The chemical composition of the glass surface is different to bulk, because there is higher concentration of surface active components (so called surfactants). Surfactants may be identified by strong negative correlation between their concentration in the bulk and the value of surface tension. In contrast, the surface tension enhancing components have a lower concentration in the surface layer than in the bulk. Oxides like MgO, ZnO, BaO, ZrO_2 , and Li_2O generally increase the surface tension of glassforming melts, other oxides, mainly K_2O , PbO and B_2O_3 , decrease it. Even a very small concentration of some oxides, especially

V_2O_5 , Cr_2O_3 , MoO_3 or WO_3 intensively reduces the surface tension of the glassforming melts [9–15].

The true chemical composition of the glass bulk may be obtained by the proper thermodynamic model, i.e. the oxide glassforming melt can't be seen as a mixture of oxides but as an equilibrium solution of system components formed by the reaction of oxides. In the thermodynamic model of Shakhmatkin and Vedishcheva (TDM, so called associated solutions model) [16–19], the glassforming melt is considered to be an equilibrium ideal mixture containing unreacted oxides and components formed by their interaction. The stoichiometry of system components is given by the compounds found in the particular equilibrium phase diagrams. The model of Shakhmatkin and Vedishcheva uses the molar Gibbs energies of system components, analytical oxide composition, and glassforming melt temperature as input data. For glasses the glass transition temperature is used. One of the advantages of this model is that it does not require any adjustable parameters. The molar Gibbs

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Table. I

Analyzed composition (mol.%) of $x\text{Na}_2\text{O}\cdot(15-x)\text{K}_2\text{O}\cdot y\text{CaO}\cdot(10-y)\text{ZnO}\cdot z\text{ZrO}_2\cdot(75-z)\text{SiO}_2$ glasses, and surface tension at 1400 °C obtained from sessile (γ_{ses}) and pendant drop profile (γ_{pen}).

x	Y	z	Glass abbrev.	Na ₂ O	K ₂ O	CaO	ZnO	ZrO ₂	SiO ₂	$\gamma_{\text{ses}} \pm 4 /$	$\gamma_{\text{pen}} \pm 4 /$
15	10	0	NCZ0	15.30	–	9.22	–	–	75.48	mN.m ⁻¹	mN.m ⁻¹
15	10	1	NCZ1	13.86	–	10.69	–	0.93	74.52	271	275
15	10	3	NCZ3	13.42	–	10.19	–	2.86	73.53	274	279
15	10	5	NCZ5	14.99	–	10.00	–	4.87	70.14	280	284
15	10	7	NCZ7	14.07	–	9.78	–	6.77	69.38	283	288
0	10	0	KCZ0	–	14.98	8.42	–	–	76.60	288	292
0	10	1	KCZ1	–	14.29	8.44	–	1.02	76.25	190	193
0	10	3	KCZ3	–	15.41	10.08	–	3.28	71.23	191	194
0	10	5	KCZ5	–	15.44	10.06	–	4.92	69.58	195	196
0	10	7	KCZ7	–	14.74	9.33	–	7.32	68.61	205	210
15	0	0	NzZ0	14.80	–	–	9.90	–	75.30	212	210
15	0	1	NzZ1	15.04	–	–	9.41	1.03	74.52	286	288
15	0	3	NzZ3	15.29	–	–	11.04	3.19	70.48	295	301
15	0	5	NzZ5	14.77	–	–	9.01	4.90	71.32	304	307
15	0	7	NzZ7	14.18	–	–	9.89	6.54	69.39	311	313
0	0	0	KzZ0	–	15.74	–	8.47	–	75.79	312	316
0	0	1	KzZ1	–	14.93	–	10.49	0.97	73.61	222	219
0	0	3	KzZ3	–	14.20	–	9.86	2.80	73.14	233	235
0	0	5	KzZ5	–	16.00	–	10.44	4.91	68.65	246	253
0	0	7	KzZ7	–	15.63	–	10.69	7.06	66.62	255	258
7.5	10	1	NKCZ1	7.64	7.36	8.61	–	0.95	75.44	–	–
7.5	10	3	NKCZ3	7.54	7.44	8.84	–	2.86	73.32	277	280
7.5	10	5	NKCZ5	7.74	6.89	9.97	–	5.12	70.28	280	284
7.5	10	7	NKCZ7	7.66	7.01	9.98	–	7.18	68.17	287	291
7.5	0	1	NKzZ1	7.45	7.41	–	10.08	0.98	74.08	292	296
7.5	0	3	NKzZ3	7.30	7.06	–	9.63	2.61	73.40	284	290
7.5	0	5	NKzZ5	7.66	7.13	–	10.92	5.22	69.07	291	294
7.5	0	7	NKzZ7	7.83	7.00	–	11.03	7.54	66.6	296	299
15	5	1	NCzZ1	13.51	–	4.80	4.58	0.89	76.22	300	301
15	5	3	NCzZ3	13.72	–	4.72	5.01	2.71	73.84	301	301
15	5	5	NCzZ5	15.78	–	5.13	5.58	5.42	68.09	306	307
15	5	7	NCzZ7	15.78	–	5.11	5.43	7.4	66.29	308	311
0	5	1	KCzZ1	–	15.81	5.03	5.27	1.01	72.88	314	318
0	5	3	KCzZ3	–	13.95	4.47	4.95	2.66	73.97	257	259
0	5	5	KCzZ5	–	13.64	4.97	5.48	5.20	70.72	264	267
0	5	7	KCzZ7	–	13.88	4.98	5.43	7.25	68.48	273	277
7.5	5	1	NKCzZ1	8.22	8.01	4.40	5.40	1.05	72.92	–	–
7.5	5	3	NKCzZ3	6.61	6.96	4.41	4.81	2.58	74.63	275	279
7.5	5	5	NKCzZ5	7.82	7.18	5.18	5.63	5.35	68.85	283	289
7.5	5	7	NKCzZ7	7.86	6.99	5.00	5.53	7.40	67.22	294	294

energies of system components can be found in various thermodynamic databases. In our case, the FACT thermodynamic database was used [20,21].

A number of methods are known for measuring the surface tension of liquids. The most common methods are based on the analysis of sessile or pendant drop profile [22–27]. The principle of these methods is based on the regression analysis of the droplet profile based on the numerical integration of the Laplace equation [28–32].

The main aim of the present work is identifying of surface active components of studied glassforming system by analysis of surface tension dependence on equilibrium molar amounts of TDM components.

Experimental part

Nine compositional series of $\text{Na}_2\text{O}\text{-K}_2\text{O}\text{-CaO}\text{-ZnO}\text{-ZrO}_2\text{-SiO}_2$ glass-forming melts were studied: $x\text{Na}_2\text{O}\cdot(15-x)\text{K}_2\text{O}\cdot y\text{CaO}\cdot(10-y)\text{ZnO}\cdot z\text{ZrO}_2\cdot(75-z)\text{SiO}_2$ ($x = 0, 15; y = 0, 10; z = 0, 1, 3, 5, 7$). Abbreviation of glasses is summarized in Table I. The proposed compositions are based on equimolar substitutions $\text{Na}_2\text{O}/\text{K}_2\text{O}$, CaO/ZnO , and $\text{ZrO}_2/\text{SiO}_2$.

The glass batches were prepared by mixing of powdered carbonates and oxides of analytical grade purity. The glasses were melted for 2–3 h in the Pt-20%Rh crucible in a super-kanthal furnace at temperature of (1500–1600) °C in ambient atmosphere. Repeated manual stirring of the melt ensured the homogeneity. The melt was then poured onto a stainless steel plate. The samples were annealed in a muffle furnace for

one hour at 550 °C, after which the furnace was switched off and the samples were allowed to cool down to the laboratory temperature. Approximately 200 gs of glass was melted for each glass composition. The glassy character of all samples was checked by XRD analysis. Chemical composition of the studied glasses was determined, after their decomposition by the mixture of HF and HClO_4 , by the inductively coupled plasma optical emission spectroscopy (VARIAN - Vista MPX / ICP-OES). Chemical composition of studied glasses is summarized in Table I.

The principle of Archimedes law was used to determine the density, ρ , of the glassforming melts by the double weighing of a platinum sphere in the air and in the melt. Obtained density temperature dependence was linear for all studied melts, e.g. $\rho = a + bT$. The a and b values are summarized in the Table II together with the standard deviation of approximation obtained by linear regression analysis.

Sessile drops were prepared from the glass cubes of approximate ($3 \times 3 \times 3$) mm³ dimensions placed on glassy carbon plate (Sigradur G®) in the atmosphere of pure nitrogen. Pendant drops were obtained by melting of the T-shape glass samples suspended in the platinum wire ring. The drop profile was recorded by the microscope CCD camera (Leitz Wetzlar Germany, type: 050–054:001 No.589) and digitized using the Lucia® or NIS Elements® software (LIM, s.r.o., Prague). The temperature at which the symmetric drop shape was reached during the sample heating at 5 °C/min was chosen as the starting temperature for recording of the drop profile. Some samples were excluded due to

Table. II

Melt density at 1400 °C, molar volume (V_m), coefficients and standard deviation of approximation, s_{apr} , of the linear temperature dependence of glassforming melt density ($\rho = a + b \cdot T$, where T is temperature in °C).

Glass	ρ (1400 °C) / $g \cdot cm^{-3}$	V_m (1400 °C) / $cm^3 \cdot mol^{-1}$	a / $g \cdot cm^{-3}$	$-10^4 \cdot b$ / $g \cdot cm^{-3} \cdot ^\circ C^{-1}$	$10^4 \cdot s_{apr}$ / $g \cdot cm^{-3}$
NCZ0	2.3026	26.060	2.4338	0.911	3.18
NCZ1	2.3458	25.793	2.5641	1.530	21.00
NCZ3	2.4124	25.591	2.4630	0.339	1.23
NCZ5	2.4794	25.426	2.5930	0.789	3.77
NCZ7	2.5324	25.365	2.7222	1.340	6.39
KCZ0	2.2852	28.381	2.4673	1.320	7.92
KCZ1	2.3192	28.141	2.4883	1.220	3.45
KCZ3	2.3846	28.100	2.6838	2.110	32.00
KCZ5	2.4416	27.873	2.5858	1.060	5.31
KCZ7	2.5026	27.715	2.9091	2.910	24.70
NzZ0	2.4158	25.860	2.5555	1.030	1.65
NzZ1	2.4778	25.435	2.6482	1.230	12.30
NzZ3	2.5298	25.590	2.8011	1.930	20.20
NzZ5	2.5760	25.379	2.7962	1.600	25.30
NzZ7	2.6338	25.282	2.8191	1.330	7.43
KzZ0	2.3892	28.150	2.6322	1.720	9.30
KzZ1	2.4324	27.965	2.6218	1.340	6.00
KzZ3	2.4720	27.830	2.7075	1.700	12.3
KzZ5	2.5482	27.810	2.8102	1.870	8.94
KzZ7	2.5990	27.760	2.8308	1.650	9.55
NKCZ1	2.3232	27.115	2.4844	1.120	14.40
NKCZ3	2.3746	27.043	2.5311	1.110	12.40
NKCZ5	2.4604	26.587	2.6156	1.140	8.49
NKCZ7	2.5130	26.563	2.7308	1.550	6.55
NKzZ1	2.4414	26.836	2.5808	0.988	5.02
NKzZ3	2.6374	25.149	2.6477	1.090	6.68
NKzZ5	2.5798	26.468	2.7766	1.430	5.36
NKzZ7	2.6388	26.425	2.8617	1.580	4.29
NCzZ1	2.3926	25.782	2.5202	0.914	11.50
NCzZ3	2.4544	25.641	2.6006	1.040	10.50
NCzZ5	2.5340	25.567	2.7283	1.400	16.10
NCzZ7	2.6056	25.335	2.8108	1.460	4.51
KCzZ1	2.3558	28.456	2.5007	1.030	7.08
KCzZ3	2.4236	27.809	2.6021	1.260	7.73
KCzZ5	2.5290	27.281	2.5461	1.150	5.32
NKCzZ1	2.3770	27.181	2.5072	0.948	2.35
NKCzZ3	2.7610	23.564	2.6031	1.150	9.25
NKCzZ5	2.5364	26.438	2.7813	1.740	15.70
NKCzZ7	2.5676	26.588	2.8045	1.660	7.83

crystallization.

The values of surface tension were obtained by minimization of the sum of squares of deviations between the experimental and calculated drop profile. The calculated drop profile was obtained by the numerical integration of the Laplace equation using the experimental density value. The own program KVAREG (in FORTRAN) was used [30]. The coordinates of individual points of the droplet profile (Figs. 1,2) and the value of glass-forming melt density at the particular temperatures

(obtained by linear interpolation of measured temperature dependence of the density of investigated melt) were used as the input data. The drop profiles were analyzed over the temperature range (1250–1500) °C [33].

For comparison the approximate surface tension values, γ^{apr} , were calculated by the commonly used formula proposed by Dorsey [34,35]:

$$\gamma^{apr} = g\rho r^2(0.052/f - 0.12268 + 0.0481f) \quad (1)$$

with

$$f = (r_{45} - h_{45})/r - 0.04142 \quad (2)$$

where g is the gravity acceleration, ρ - density, r - the drop equatorial radius, and r_{45} and h_{45} are the drop radius and height from the level of 45° tangent (see Fig. 3).

Results and discussion

Chemical composition of the studied glasses measured by the inductively coupled plasma optical emission spectroscopy is summarized in the Table I. The differences between theoretical and real compositions reaching typically (1–2) mol.% were found to be acceptable. These differences are probably caused by volatilization of the alkaline oxides.

Obtained density temperature dependence was linear for all studied melts, e.g. $\rho = a + b \cdot T$. The a and b values are summarized in the Table II together with the standard deviation of approximation indicating the almost ideal linearity (on the level of measurement experimental error). Moreover, the density and molar volume at 1400 °C are reported in the Table II. Significant increase in density caused by the ZrO_2/SiO_2 substitution was identified. It can be also stated that the densities of potassium glasses are lower than the densities of analogous sodium glasses. This is a result of significant increase of molar volume caused by K_2O/Na_2O substitution. On the other hand, the densities of zinc glasses are higher than the densities of analogous calcium glasses.

The experimental values of surface tension obtained for sessile and pendant drop are compared in Table III for five- and six-component glassforming melts. On the basis of repeated measurements the mean experimental error was estimated on the level of $4 \text{ mN} \cdot \text{m}^{-1}$. Moreover the approximate values obtained for sessile drop using the Dorsey's method (Eqs.(1–2)) are reported. By comparing the surface tensions obtained by the method of sessile and pendant drop, we can confirm that both methods are sufficiently accurate. The surface tension values obtained from the pendant drop profile are systematically higher (on the level of 1–2 relative%) than corresponding values obtained from sessile drop profile. It should be emphasized that the correctness of the sessile drop method is also conditioned by the horizontality of the substrate, guaranteeing the rotational symmetry of the droplet. This factor was partially eliminated by separately evaluating the left and right profiles of the drop and using of the mean value for surface tension evaluation. Thus, the experimentally more difficult method of

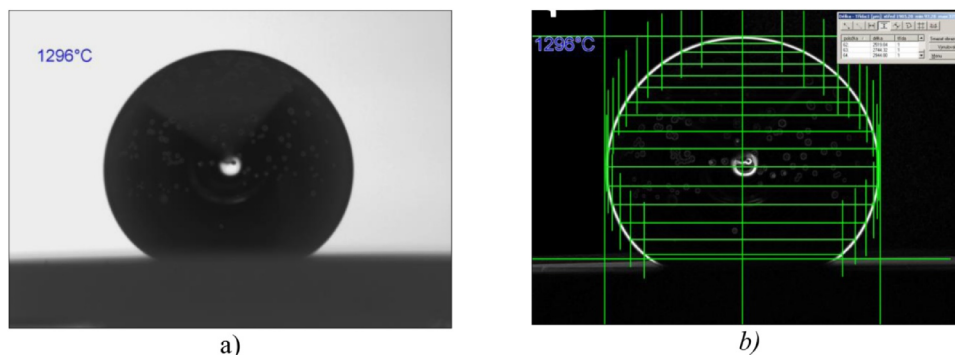


Fig. 1. Sessile drop profile (NCZ1) a) captured by a digital camera, b) after processing with LUCIA G software.

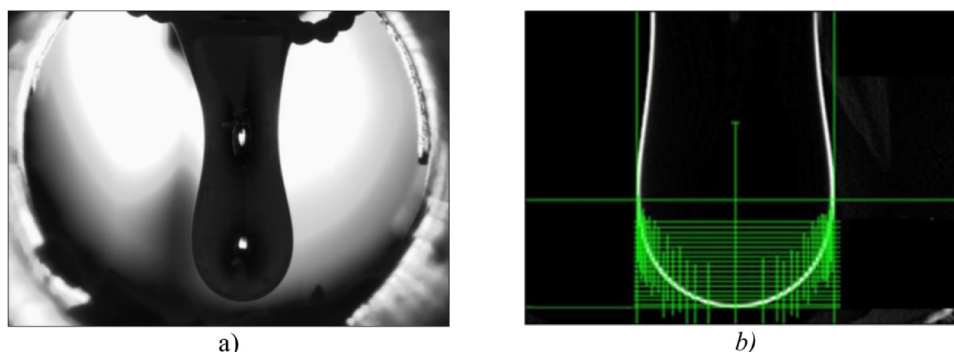


Fig. 2. Pendant drop profile (KzZO) a) captured by digital camera, b) after processing by LUCIA G software.

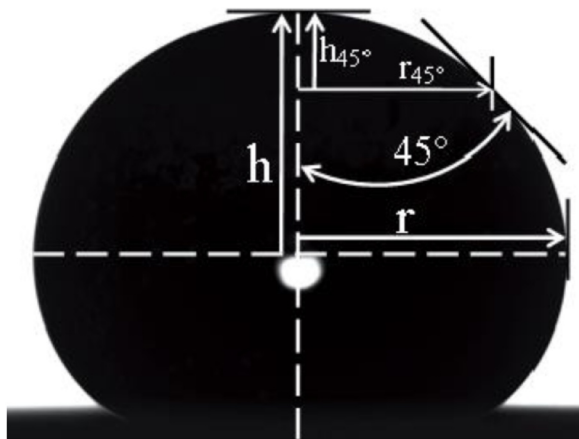


Fig. 3. Coordinates used for the Dorsey's approximate method Eqs. (1), (2).

Table III

Experimental values of melt density ρ at temperature t , comparison of surface tension values determined from the sessile (γ_{ses}^{exp}) and pendant (γ_{pen}^{exp}) drop profile, and calculated by Dorsey's method (γ_{ses}^{apr}), for 5- and 6-component glasses.

Glass	T/C	$\rho/g, cm^{-3}$	$\gamma_{ses}^{exp}/mN, m^{-1}$	$\gamma_{ses}^{apr}/mN, m^{-1}$	$\gamma_{pen}^{exp}/mN, m^{-1}$
NKCZ1	1371	2.3309	279	280	282
NKCZ3	1372	2.3796	280	284	285
NKCZ5	1353	2.4618	289	293	294
NKCZ7	1353	2.5216	294	296	300
NKzZ1	1371	2.4451	285	291	291
NKzZ3	1373	2.4980	293	296	295
NKzZ5	1396	2.5767	296	301	299
NKzZ7	1355	2.6486	303	308	304
NCzZ1	1371	2.3940	303	306	303
NCzZ3	1371	2.4587	306	309	308
NCzZ5	1350	2.5368	310	313	314
NCzZ7	1352	2.6129	316	317	320
KCzZ1	1373	2.3586	257	261	260
KCzZ3	1373	2.4296	265	269	270
KCzZ5	1381	2.3855	274	278	278
NKCzZ1	1372	2.3768	275	277	280
NKCzZ3	1373	2.4458	285	289	291
NKCzZ5	1350	2.5465	296	300	297

pendant drop appears to be more reliable. Moreover, it can be seen that the approximate Dorsey's values are little bit higher than the values obtained from sessile drop profile and little bit lower than the values obtained from pendant drop profile.

The linear temperature dependence of the surface tension determined by the sessile and pendant drop method was found for all glass compositions. The coefficients of the linear dependence ($\gamma = A + B \cdot T$) are summarized in the Table IV together with the standard deviation of approximation.

It can be seen (Table IV) that the surface tension monotonously increases by the equimolar substitution of ZrO_2 for SiO_2 . Moreover, significant decrease in surface tension was observed by increasing the content of potassium oxide K_2O by the equimolar Na_2O/K_2O substitution. However, in the first step (i.e. decreasing the Na_2O content from 15 mol.% to 7.5 mol.%) the change of surface tension is for glasses containing 10 mol.% CaO almost negligible (i.e. NCZi versus NKZi, $i \equiv 1,3,5,7$). On the other hand the effect the equimolar CaO/ZnO substitution is not monotonous. In the first step (decreasing of CaO content from 10 mol.% to 5 mol.%) the surface tension significantly increases (e.g. KCZi versus KCzZi, $i \equiv 1,3,5,7$) while in the second step (decreasing of CaO content from 5 mol.% to 0 mol.%) the surface tension significantly decreases (e.g. KCzZi versus KzZi, $i \equiv 1,3,5,7$). Thus on the level of oxide composition the compositional dependence of surface tension cannot be simply quantified. This can be explained by the fact, that surface active are not the single oxides but their compounds.

Thermodynamic model of Shakhmatkin and Vedishcheva was used to investigate the compositional dependence surface tension. Molar Gibbs energies of the components needed as input data for the TDM were obtained from the FACT database. The own JaneDove FORTRAN program was used to calculate equilibrium composition for each glass melt at 1400 °C. The total number of 36 system components was considered. The following ten components were found with negligible equilibrium molar abundance in all glasses: K_2O , Na_2O , C3S ($3CaO \cdot 3SiO_2$), N2S ($2Na_2O \cdot SiO_2$), N3S2 ($3Na_2O \cdot 3SiO_2$), C6Zr19 ($6CaO \cdot 19ZrO_2$), K2S ($2K_2O \cdot SiO_2$), N5S ($5Na_2O \cdot SiO_2$), NZn ($Na_2O \cdot ZnO$), N4C3S5 ($4Na_2O \cdot 3CaO \cdot 5SiO_2$). Threshold of $5 \cdot 10^{-7}$ mol was applied for quantification of significant species abundance. Thus, only 26 components were present with not negligible equilibrium amount – these are summarized in Table V. Correlation analysis found the high positive correlations between equilibrium molar amounts of following system components:

CaO – C2S – C3S2 – CS – only C2S was considered in regression analysis (to avoid the singularity), i.e. C2S represents the equilibrium mixture of CaO, C2S, C3S2, and CS;

ZnO – Zn2S – only ZnO was considered in regression analysis;

ZrO2 – ZrS – only ZrO_2 was considered in regression analysis;

CZr – C3ZrS2 – only CZr was considered in regression analysis;

KS2 – KS4 – KS – only KS4 was considered in regression analysis;

NC2S3 – NC3S6 – NC2S2 – NCS – only NC2S3 was considered in regression analysis;

NS2 – N3S8 – NS – only N3S8 was considered in regression analysis.

The surface tensions for sessile and pendant drop were described by multilinear regression equation:

$$\gamma = \sum_{i=1}^{13} a_i n_i \quad (3)$$

Multilinear regression analysis was used for obtaining the estimates of the a_i ($i = 1, 2, \dots, 13$) parameters together with their standard deviations. The statistical significance of estimates was determined on the

Table. IV

Coefficients and standard deviation of approximation, s_{appr} , of the linear temperature dependence of surface tension measured by sessile and pendant drop method ($\gamma = A + B \cdot T$, where T is temperature in °C).

Glass	$A_{\text{ses}} / \text{mN} \cdot \text{m}^{-1}$	$-10^3 \cdot B_{\text{ses}} / \text{mN} \cdot \text{m}^{-1} \cdot \text{°C}^{-1}$	$s_{\text{appr}} / \text{mN} \cdot \text{m}^{-1}$	$A_{\text{pen}} / \text{mN} \cdot \text{m}^{-1}$	$-10^3 \cdot B_{\text{pen}} / \text{mN} \cdot \text{m}^{-1} \cdot \text{°C}^{-1}$	$s_{\text{appr}} / \text{mN} \cdot \text{m}^{-1}$
NCZ0	460	134	0.65	488	152	1.34
NCZ1	411	98	0.61	424	103	1.09
NCZ3	405	89	0.17	421	98	0.62
NCZ5	394	79	0.39	372	60	0.38
NCZ7	401	81	0.06	427	96	1.24
KCZ0	271	58	0.41	277	60	0.80
KCZ1	284	66	0.68	324	93	1.02
KCZ3	278	59	0.48	303	76	0.23
KCZ5	304	71	0.40	288	56	0.99
KCZ7	336	89	0.00	275	45	0.00
NzZ0	413	91	0.48	420	94	1.30
NzZ1	398	73	0.63	404	73	0.98
NzZ3	409	75	0.64	409	73	0.82
NzZ5	374	45	0.11	397	60	0.33
NzZ7	419	77	0.61	439	88	0.49
KzZ0	474	180	1.99	476	184	2.24
KzZ1	450	155	1.96	540	218	1.40
KzZ3	530	202	2.41	506	181	0.01
KzZ5	430	125	1.55	451	138	0.19
NKCZ1	353	55	0.41	362	59	0.15
NKCZ3	337	41	0.60	358	53	0.15
NKCZ5	333	32	0.41	371	57	0.66
NKCZ7	361	49	0.65	406	79	0.40
NKzZ1	367	59	0.68	360	50	0.23
NKzZ3	357	47	0.49	365	51	0.06
NKzZ5	405	78	0.18	387	63	0.00
NKzZ7	387	63	0.31	387	62	0.31
NCzZ1	376	53	0.39	406	75	0.68
NCzZ3	366	43	0.59	395	63	0.44
NCzZ5	391	59	0.92	400	64	0.33
NCzZ7	383	49	0.16	390	52	0.12
KCzZ1	323	47	0.81	338	56	0.27
KCzZ3	340	55	0.52	362	67	0.99
KCzZ5	360	62	0.24	336	42	0.00
NKCzZ1	343	48	1.11	356	55	0.06
NKCzZ3	368	61	0.27	357	48	0.65
NKCzZ5	359	47	0.28	383	63	0.58

Table. V

TDM components with not negligible equilibrium abundance. Components with uncorrelated abundance in studied glasses are numbered and emphasized by bold.

No.	Stoichiometry	Abbreviate	No.
			uncorrel.
1.	CaO	CaO	1.
2.	SiO ₂	SiO ₂	2.
3.	ZnO	ZnO	3.
4.	ZrO ₂	ZrO ₂	4.
5.	C2S	2CaO.SiO ₂	5.
6.	C2ZnS2	2CaO.ZnO ₂ .2SiO ₂	6.
7.	C3S2	3CaO.2SiO ₂	7.
8.	CS	CaO.SiO ₂	8.
9.	CZr	CaO.ZrO ₂	9.
10.	KS2	K ₂ O.2SiO ₂	10.
11.	KS4	K ₂ O.4SiO ₂	11.
12.	KS	K ₂ O.SiO ₂	12.
13.	NC2S3	Na ₂ O.2CaO.3SiO ₂	13.
14.	NC3S6	Na ₂ O.3CaO.6SiO ₂	
15.	NCS5	Na ₂ O.CaO.5SiO ₂	
16.	NS2	Na ₂ O.2SiO ₂	
17.	N2CS3	2Na ₂ O.CaO.3SiO ₂	
18.	N3S8	3Na ₂ O.8SiO ₂	
19.	Zn2S	2ZnO.SiO ₂	
20.	ZrS	ZrO ₂ .SiO ₂	
21.	NS	Na ₂ O.SiO ₂	
22.	C2ZrS4	2CaO.ZrO ₂ .4SiO ₂	
23.	C3ZrS2	3CaO.ZrO ₂ .2SiO ₂	
24.	CZr4	CaO.4ZrO ₂	
25.	NC2S2	Na ₂ O.2CaO.2SiO ₂	
26.	NCS	Na ₂ O.CaO.SiO ₂	

Table. VI

Results of the multilinear regression analysis (Eq. (3)), s_{appr} - standard deviation of approximation, r - correlation coefficient, F - Fischer's F-statistics. Surface active components are emphasized by bold characters.

Comp.	Value	$\gamma_{\text{ses}} / \text{mN} \cdot \text{m}^{-1} \cdot \text{mol}^{-1}$	$\gamma_{\text{pen}} / \text{mN} \cdot \text{m}^{-1} \cdot \text{mol}^{-1}$
CaO	a_1	-	-
SiO ₂	a_2	418 ± 19	424 ± 19
ZnO	a_3	448 ± 66	441 ± 66
ZrO ₂	a_4	445 ± 93	451 ± 94
C2ZnS2	a_5	22 710 ± 2 682	22 635 ± 2 707
CZr	a_6	-	-
KS4	a_7	-1 311 ± 152	-1 328 ± 153
NC2S3	a_8	76 185 ± 9 576	79 858 ± 9 666
NCS5	a_9	-5 112 ± 983	-5 359 ± 992
N2CS3	a_{10}	-	-
N3S8	a_{11}	-37 538 ± 8 040	-38 167 ± 8 115
C2ZrS4	a_{12}	-32 096 ± 11 387	-34 226 ± 11 494
CZr4	a_{13}	-	-
	$s_{\text{appr}} / \text{mN} \cdot \text{m}^{-1}$	7.76	7.83
	R	0.99	0.99
	F	5 100	5 122

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 Table VI. Only the statistically significant components were taken into account (a_1 , a_6 , a_{10} , and a_{13} were statistically not significant). The surface active components were identified by negative a_i values. Such way the N3S8 and C2ZrS4 were identified as "strongly" surface active and NCS5 and KS4 as probably surface active (due to one order lower

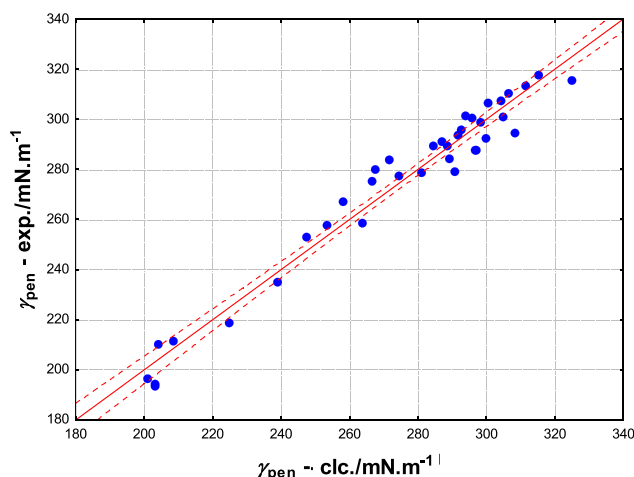
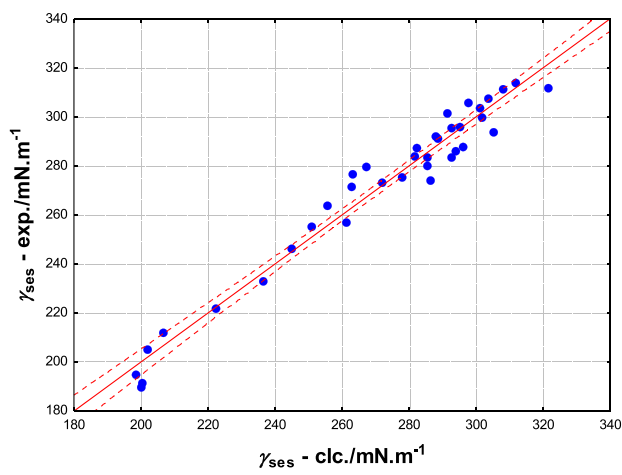


Fig. 4. Experimental versus calculated (Eq. (3), Table VI) values of surface tension for sessile and pendant drop (points). The $\gamma - \text{exp} = \gamma - \text{clc}$ is represented by the full line. Dotted lines represent the 95% confidence limit.

absolute a_i value). It is worth noting that KS4 represents the equilibrium mixture of KS2, KS4, and KS with strongly positive correlated equilibrium abundance. Similarly N3S8 represents a mixture of NS2, N3S8, and NS. The experimental and calculated values are compared in Fig. 4. It can be seen that the results for pendant and sessile drop are practically equivalent. The standard deviation of approximation approaches the level of experimental error in both cases.

Conclusions

Surface tension of glasses with compositions of $x\text{Na}_2\text{O} \cdot (15-x)\text{K}_2\text{O} \cdot y\text{CaO} \cdot (10-y)\text{ZnO} \cdot z\text{ZrO}_2 \cdot (75-I)\text{SiO}_2$ ($x = 0, 15; y = 0, 10; z = 0, 1, 3, 5, 7$) were measured over the (1250–1500) °C temperature range by the sessile and pendant drop methods using the melt density value obtained by independent experiment. Linear temperature decrease of the measured surface tension was found for all studied glass melts. On the level of oxide composition the compositional dependence of surface tension cannot be simply quantified. This can be explained by the fact, that surface active are not the single oxides but their compounds.

The compositional dependence of the surface tension was described as multilinear function of equilibrium molar amounts of not negligible and uncorrelated components of Shakhmatkin and Vedishcheva thermodynamic model with the accuracy on the level of experimental error. Such way the N3S8 (representing the equilibrium mixture of NS2, N3S8, and NS) and C2ZrS4 were identified as “strongly” surface active and NCS5 and KS4 (representing the equilibrium mixture of KS2, KS4, and KS) as probably surface active.

Author statement

Maria Chromčíková, Branislav Hruška Roman Svoboda, Marek Liška, Aleksandra Nowicka, Els Bruneel, Klaartje De Buysser - performed experiments and, analysed data and co-wrote the paper.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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