



Title	Surface Tension Evaluation of Molten Silicates Containing Surface-active Components (B_20_3, CaF_2 or Na_2O)
Author(s)	Nakamoto, Masashi; Tanaka, Toshihiro; Holappa, Lauri et al.
Citation	ISIJ International. 2007, 47(2), p. 211-216
Version Type	VoR
URL	<a href="https://hdl.handle.net/11094/26405">https://hdl.handle.net/11094/26405</a>
rights	© 2007 ISIJ
Note	

*The University of Osaka Institutional Knowledge Archive : OUKA*

<https://ir.library.osaka-u.ac.jp/>

The University of Osaka

# Surface Tension Evaluation of Molten Silicates Containing Surface-active Components ( $B_2O_3$ , $CaF_2$ or $Na_2O$ )

Masashi NAKAMOTO,<sup>1)</sup> Toshihiro TANAKA,<sup>2)</sup> Lauri HOLAPPA<sup>1)</sup> and Marko HÄMÄLÄINEN<sup>3)</sup>

1) Laboratory of Metallurgy, Helsinki University of Technology, P.O. Box 6200, FIN-02015 TKK, Espoo, Finland.

2) Division of Materials and Manufacturing Science, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871 Japan.

3) Laboratory of Material Processing and Powder Metallurgy, Helsinki University of Technology, P.O. Box 6200, FIN-02015 TKK, Espoo, Finland.

(Received on October 2, 2006; accepted on November 21, 2006)

A thermodynamic model for determining the surface tension of molten ionic mixtures, derived by considering the ionic radii, was applied to molten silicates containing a surface-active component  $B_2O_3$ ,  $CaF_2$  or  $Na_2O$ . The calculated results of the present model were in agreement with the experimental data in these ternary systems over a wide temperature range.

KEY WORDS: surface tension; thermodynamic; silicate; ionic radius;  $B_2O_3$ ;  $CaF_2$ ;  $Na_2O$ ; surface-active component.

## 1. Introduction

The surface tension of silicate melts plays important roles in the processes at high temperature. For example, it is said that the most effective physical properties of mold flux in continuous-casting processes include, surface tension (interfacial tension), viscosity and solidification temperature.<sup>1,2)</sup> Mold fluxes usually comprise about 70% ( $CaO + SiO_2$ ), 0–6%  $MgO$ , 2–6%  $Al_2O_3$ , 2–10% ( $Na_2O + K_2O$ ), 0–10%  $F$ , with varying amounts of  $B_2O_3$ ,  $TiO_2$ ,  $ZrO_2$ ,  $Li_2O$  and  $MnO$ .<sup>2)</sup> The  $CaF_2$  and  $Na_2O$  components are known to behave as network modifiers in mold fluxes, and can drastically alter the network structures of siliceous mold fluxes, affecting their physical properties.  $B_2O_3$  is also interesting from the viewpoint that the triangular  $BO_3^{3-}$  ions exist within network structures in the melt phase, and the surface tension of molten silicates containing  $B_2O_3$  is one of the most important physical properties for understanding the foam formation *etc.* in the industrial processes for borosilicate glasses.<sup>3)</sup>

In addition, the surface-active constituents  $B_2O_3$ ,  $CaF_2$  and  $Na_2O$  are fascinating components in the respect of constructing models for evaluating the surface tension of molten slag.<sup>4,5)</sup> Mills and Keene<sup>4)</sup> insist on the difficulties of the modeling of surface tension in the slag systems including surface-active constituents, since these are known to migrate preferentially to the surface and cause a sharp decrease in the surface tension. Some models<sup>4–6)</sup> have been developed for evaluating the surface tension of molten slag containing surface-active components. Mills and Keene<sup>4)</sup> modified Boni and Derge's model<sup>6)</sup> based on the additivity rule for the surface tension of multi-component slags by considering the effect of surface-active constituents on the surface tension. They assumed that the effect of surface-active

constituents on the surface tension changes with concentration, and applied polynomial expressions to the surface tensions of those constituents accordingly. However, Mills and Keene pointed out that their model tends to overestimate the decrease in surface tension of slag systems containing more than one surface-active component. Nakajima<sup>5)</sup> proposed an expanded set of approximation rules constructed on the basis of the regular solution approximation of excess molar quantities for binary silicate melts, in order to estimate surface tension in multi-component silicate systems containing  $CaF_2$  and  $Na_2O$ . Although this model predicted the experimental data well in some molten silicates containing surface-active components, there is a certain limitation with respect to the composition ranges in which the regular solution approximation rules can be applied, such that several parameters have to be estimated.

Tanaka *et al.*<sup>7–11)</sup> applied thermodynamic databases to evaluate the surface tensions of liquid alloys, ionic melts and oxide melts by using a model based on Butler's equation.<sup>12)</sup> Although the calculated results were in good agreement with the experimental data, the applicability of this model to evaluate the surface tension of oxide melts was limited due to a lack of thermodynamic data for these particular multi-component systems. Recently, Tanaka *et al.*<sup>13)</sup> have developed a new model for evaluating the surface tension of molten silicates, which takes into consideration the ionic radii of the components. This particular model can be readily applied to many kinds of molten ionic mixtures and molten slags, because the surface tension of silicate melts can be calculated using the information on the surface tensions and molar volumes of pure oxides, as well as the cationic and anionic radii of the component oxides in the system. This model has already been applied to the calculations of surface tension for several ternary silicate melts

comprising  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{FeO}$ ,  $\text{MgO}$  or  $\text{MnO}$ .<sup>14)</sup> The obtained results reproduced the composition dependence of the surface tension in a wide range of ternary systems. In the present work, applied this model was to evaluate the surface tension of silicate melts containing the following surface-active components,  $\text{B}_2\text{O}_3$ ,  $\text{CaF}_2$  or  $\text{Na}_2\text{O}$ .

## 2. Model for Evaluating Surface Tension of Molten AX–BY–CZ System

The Eqs. (1), (2) and (3) for evaluating the surface tension ( $\sigma$ ) of the AX–BY–CZ melts have been derived from Butler's equation<sup>12)</sup> by considering the assumptions [1] and [2].<sup>13,14)</sup>

[1] It is well known that molten ionic mixtures readily undergo surface relaxation processes, such as spontaneous changes in ionic distance at the surface, which enables the energetic state of the surface to approach that of the bulk state. Thus, the contribution from excess Gibbs energy terms is neglected.

[2] In ionic substances, it is well known that their ionic structures depend upon the ratio of the cationic to anionic radii. Therefore, in order to evaluate the ionic structures and physico-chemical properties of ionic materials, we should consider the cationic to anionic radii ratio.

$$\sigma = \sigma_{\text{AX}}^{\text{Pure}} + \frac{RT}{A_{\text{AX}}} \ln \frac{M_{\text{AX}}^{\text{Surf}}}{M_{\text{AX}}^{\text{Bulk}}} \quad \text{.....(1)}$$

$$\sigma = \sigma_{\text{BY}}^{\text{Pure}} + \frac{RT}{A_{\text{BY}}} \ln \frac{M_{\text{BY}}^{\text{Surf}}}{M_{\text{BY}}^{\text{Bulk}}} \quad \text{.....(2)}$$

$$\sigma = \sigma_{\text{CZ}}^{\text{Pure}} + \frac{RT}{A_{\text{CZ}}} \ln \frac{M_{\text{CZ}}^{\text{Surf}}}{M_{\text{CZ}}^{\text{Bulk}}} \quad \text{.....(3)}$$

where

$$M_{\text{AX}}^{\text{P}} = \frac{\frac{R_{\text{A}}}{R_{\text{X}}} \cdot N_{\text{AX}}^{\text{P}}}{\frac{R_{\text{A}}}{R_{\text{X}}} \cdot N_{\text{AX}}^{\text{P}} + \frac{R_{\text{B}}}{R_{\text{Y}}} \cdot N_{\text{BY}}^{\text{P}} + \frac{R_{\text{C}}}{R_{\text{Z}}} \cdot N_{\text{CZ}}^{\text{P}}},$$

$$M_{\text{BY}}^{\text{P}} = \frac{\frac{R_{\text{B}}}{R_{\text{Y}}} \cdot N_{\text{BY}}^{\text{P}}}{\frac{R_{\text{A}}}{R_{\text{X}}} \cdot N_{\text{AX}}^{\text{P}} + \frac{R_{\text{B}}}{R_{\text{Y}}} \cdot N_{\text{BY}}^{\text{P}} + \frac{R_{\text{C}}}{R_{\text{Z}}} \cdot N_{\text{CZ}}^{\text{P}}},$$

$$M_{\text{CZ}}^{\text{P}} = \frac{\frac{R_{\text{C}}}{R_{\text{Z}}} \cdot N_{\text{CZ}}^{\text{P}}}{\frac{R_{\text{A}}}{R_{\text{X}}} \cdot N_{\text{AX}}^{\text{P}} + \frac{R_{\text{B}}}{R_{\text{Y}}} \cdot N_{\text{BY}}^{\text{P}} + \frac{R_{\text{C}}}{R_{\text{Z}}} \cdot N_{\text{CZ}}^{\text{P}}}$$

Subscripts A, B and C correspond to cations, while X, Y and Z correspond to anions.  $R$  is the gas constant,  $T$  is the absolute temperature.  $\sigma_i^{\text{Pure}}$  is the surface tension of pure molten compound  $i$  ( $i = \text{AX}, \text{BY}$  or  $\text{CZ}$ ), which is treated as a model parameter.  $A_i = N_0^{1/3} \cdot V_i^{2/3}$  corresponds to the molar surface area in a monolayer of pure molten compound  $i$  ( $N_0$ : Avogadro's number,  $V_i$ : molar volume of pure molten oxide  $i$ ).  $N_i^{\text{P}}$  is the mole fraction of compound  $i$  in phase P ( $\text{P} = \text{Surf}$  or  $\text{Bulk}$ ). 'Surf' and 'Bulk' indicate the surface and the bulk, respectively.  $R_{\text{A}}$ ,  $R_{\text{B}}$  and  $R_{\text{C}}$  correspond to the

radii of cations A, B and C, while  $R_{\text{X}}$ ,  $R_{\text{Y}}$  and  $R_{\text{Z}}$  correspond to the radii of anions X, Y and Z. For example, in the case of the  $\text{SiO}_2$ – $\text{CaO}$ – $\text{MgO}$  system:

$$R_{\text{A}} = R_{\text{Si}^{4+}}, \quad R_{\text{B}} = R_{\text{Ca}^{2+}}, \quad R_{\text{C}} = R_{\text{Mg}^{2+}} \quad \text{.....(4)}$$

$$R_{\text{X}} = R_{\text{SiO}_4^{4-}}, \quad R_{\text{Y}} = R_{\text{O}^{2-}}, \quad R_{\text{Z}} = R_{\text{O}^{2-}} \quad \text{.....(5)}$$

where  $\text{SiO}_4^{4-}$  is considered to be the minimum anionic unit in  $\text{SiO}_2$ . Although there is no precise information on the value of  $R_{\text{SiO}_4^{4-}}$ , the value  $R_{\text{Si}^{4+}}/R_{\text{SiO}_4^{4-}} = 0.5$ , as assessed in the previous work<sup>13,14)</sup> was used in this study. Here,  $\text{B}_2\text{O}_3$  glass melts are considered to be constructed from  $\text{BO}_3^{3-}$  units.<sup>15–19)</sup> Therefore, we must assume that the ratio of cationic to anionic radii for  $\text{B}_2\text{O}_3$  is  $R_{\text{B}^{3+}}/R_{\text{BO}_3^{3-}}$ , and treat it as a parameter in this model, as well as in  $\text{SiO}_2$ , due to a lack of information about the effective radius of  $R_{\text{BO}_3^{3-}}$ . On the other hand, an exceptional treatment is not necessary in the case of  $\text{CaF}_2$  since it is generally recognized that  $\text{F}^-$  in the silicate melts is not coordinated to  $\text{Si}^{4+}$ , which means that  $\text{CaF}_2$  is merely dissociated in the molten silicate. This was stated experimentally by several researchers.<sup>20–28)</sup> The ionic radii data were extracted from the database compiled by Shannon,<sup>29)</sup> while the molar volumes of the pure oxides (except  $\text{B}_2\text{O}_3$ ), as recommended by Mills and Keene,<sup>4)</sup> were used in the present calculations. The equation to determine the temperature dependence for the molar volume of pure  $\text{B}_2\text{O}_3$  was considered on the basis of the  $\text{B}_2\text{O}_3$  melting point<sup>30)</sup> and the recommended temperature dependence of molar volume (0.01%/K).<sup>4)</sup> The ionic radii and molar volumes are listed in **Tables 1** and **2**, respectively.

## 3. Results and Discussions

The temperature dependences of the surface tensions for pure  $\text{SiO}_2$ ,  $\text{B}_2\text{O}_3$  and  $\text{CaF}_2$ , as suggested by NIST,<sup>31)</sup> were used for the calculations in this study, since there is a large volume of surface tension measurements for these components.<sup>32,33)</sup> Due to a lack of surface tension data for pure

**Table 1.** Cationic and anionic radii (Å).<sup>29)</sup>

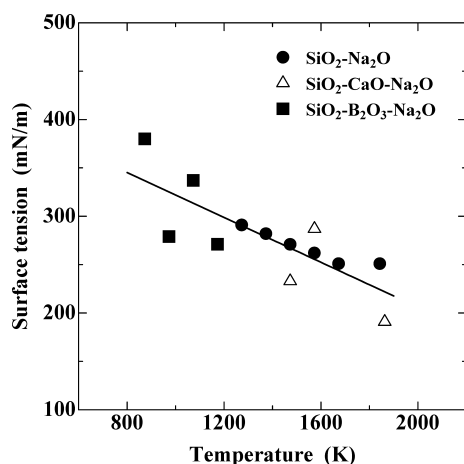
$\text{Si}^{4+}$	0.42
$\text{B}^{3+}$	0.23
$\text{Ca}^{2+}$	0.99
$\text{Na}^+$	0.97
$\text{F}^-$	1.33
$\text{O}^{2-}$	1.44

**Table 2.** Molar volume of pure component ( $\text{m}^3/\text{mol}$ ).<sup>4,30)</sup>

Oxide	Temperature (K) dependence of molar volume ( $\text{m}^3/\text{mol}$ )
$\text{SiO}_2$	$27.516 \{ 1 + 1 \cdot 10^{-4} (T - 1773) \} \cdot 10^{-6}$
$\text{B}_2\text{O}_3$	$45.8 \{ 1 + 1 \cdot 10^{-4} (T - 723) \} \cdot 10^{-6}$
$\text{CaF}_2$	$31.3 \{ 1 + 1 \cdot 10^{-4} (T - 1773) \} \cdot 10^{-6}$
$\text{CaO}$	$20.7 \{ 1 + 1 \cdot 10^{-4} (T - 1773) \} \cdot 10^{-6}$
$\text{Na}_2\text{O}$	$33.0 \{ 1 + 1 \cdot 10^{-4} (T - 1773) \} \cdot 10^{-6}$

**Table 3.** Model parameters (temperature dependences of surface tension for pure oxides).\* NIST,<sup>31)</sup> \*\* previous work<sup>14)</sup> and \*\*\* present work.

Oxide	Temperature dependence (K) of surface tension (mN/m)	
SiO <sub>2</sub> *	243.2 + 0.0317 T	1773-2073 K
B <sub>2</sub> O <sub>3</sub> *	37.9 + 0.03547 T	973-1673 K
CaF <sub>2</sub> *	1604.6 - 0.72 T	1670-1880 K
CaO**	791 - 0.0935 T	1573 - 1873 K
Na <sub>2</sub> O***	438 - 0.116 T	873 - 1863 K

**Fig. 1.** Evaluated surface tension of pure Na<sub>2</sub>O.

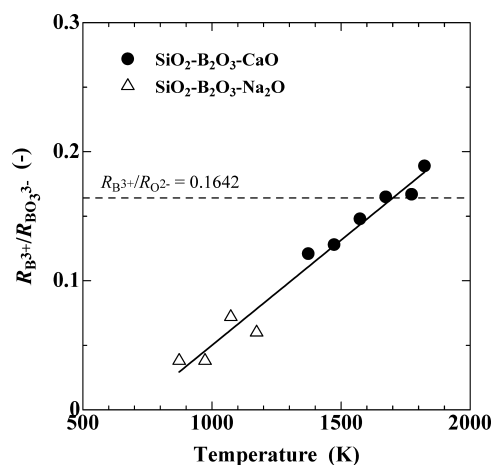
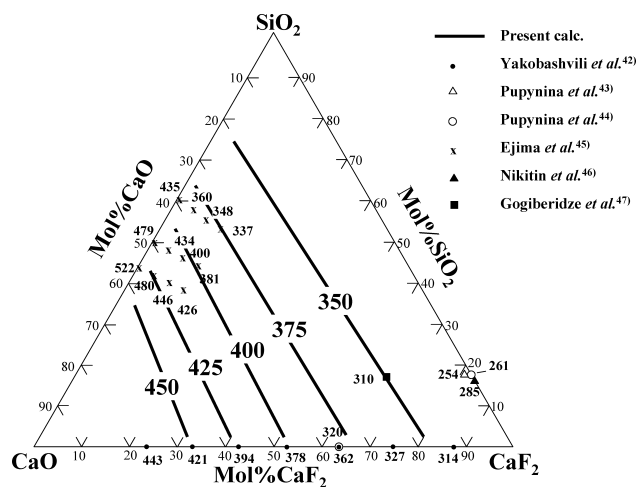
Na<sub>2</sub>O, the temperature dependent surface tension of this component was evaluated from the literature values for the binary and ternary systems containing Na<sub>2</sub>O.<sup>6,18,32,34-41)</sup> For this purpose, the following systems and temperatures were selected:

- SiO<sub>2</sub>-Na<sub>2</sub>O at 1273, 1373, 1473, 1573, 1673 and 1843 K
- SiO<sub>2</sub>-CaO-Na<sub>2</sub>O at 1473, 1573 and 1863 K
- SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O at 873, 973, 1073 and 1173 K

The temperature dependent surface tension for pure CaO evaluated in the previous work<sup>14)</sup> was also used in this study. The equations for the temperature dependent surface tensions of these components are listed in **Table 3**. In addition, the cationic to anionic radii ratios for B<sub>2</sub>O<sub>3</sub> ( $R_{B^{3+}}/R_{BO_3^{3-}}$ ) have been assessed in the present model. Therefore, the surface tensions for pure Na<sub>2</sub>O and  $R_{B^{3+}}/R_{BO_3^{3-}}$  were determined simultaneously by fitting the calculated values to the experimental values only in the SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O system.<sup>18)</sup> The SiO<sub>2</sub>-CaO-B<sub>2</sub>O<sub>3</sub> system at 1373, 1473, 1573, 1673, 1773 and 1823 K<sup>16)</sup> was also used for determining  $R_{B^{3+}}/R_{BO_3^{3-}}$ .

The surface tensions for pure Na<sub>2</sub>O, obtained from the evaluations in the silicate systems containing Na<sub>2</sub>O, are plotted in **Fig. 1**. These surface tensions were obtained by minimizing the average error between the calculated results and literature values,<sup>6,18,32,34-41)</sup> as expressed by Eq. (6) for each system temperature.

$$\text{Average error} = \frac{1}{N} \sum_{i=1}^N \left| \frac{\sigma_{\text{Calc}} - \sigma_{\text{Expe}}}{\sigma_{\text{Expe}}} \right| \times 100 (\%) \dots (6)$$

**Fig. 2.** Relationship between  $R_{B^{3+}}/R_{BO_3^{3-}}$  and temperature.**Fig. 3.** Surface tension of molten SiO<sub>2</sub>-CaO-CaF<sub>2</sub> system at 1773 K.

$\sigma_{\text{Expe}}$  and  $\sigma_{\text{Calc}}$  are the experimental and calculated surface tensions, respectively, while  $N$  is the number of the literature data in the system. The results for  $\sigma_{\text{Na}_2\text{O}}$  reasonably satisfy a linear relation with temperature, and  $\sigma_{\text{Na}_2\text{O}} = 438 - 0.116T$  was obtained as the temperature dependent surface tension of pure Na<sub>2</sub>O. **Figure 2** shows the relation between the temperature and  $R_{B^{3+}}/R_{BO_3^{3-}}$  from the evaluations of the SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O and SiO<sub>2</sub>-CaO-B<sub>2</sub>O<sub>3</sub> systems. From this figure, it is found that  $R_{B^{3+}}/R_{BO_3^{3-}}$  is dependent on temperature. Scholze<sup>15)</sup> proposed that the orientation distribution of  $BO_3^{3-}$  at the surface changes with temperature and therefore leads to a positive temperature dependent surface tension for pure B<sub>2</sub>O<sub>3</sub>. On the basis of investigations by nuclear magnetic resonance, Maekawa *et al.*<sup>19)</sup> reported that the connectivity of  $BO_3^{3-}$  units in the structure of molten B<sub>2</sub>O<sub>3</sub> has a certain temperature dependency. Although there is no exact knowledge about the structural change at the surface of B<sub>2</sub>O<sub>3</sub> melts with increasing temperature, it is considered that the results of  $R_{B^{3+}}/R_{BO_3^{3-}}$  reflect the temperature dependence of the B<sub>2</sub>O<sub>3</sub> surface structure. Therefore, we presume that a linear relation exists between  $R_{B^{3+}}/R_{BO_3^{3-}}$  and temperature, and used the formula  $R_{B^{3+}}/R_{BO_3^{3-}} = -0.113 + 1.63 \cdot 10^{-4} T$  ( $873 < T < 1823$  K) determined from Fig. 2 for the calculations in the present work. There is a possibility that the cationic and anionic radii ratio ( $R_{Si^{4+}}/R_{SiO_4^{4-}}$ ) for SiO<sub>2</sub> also

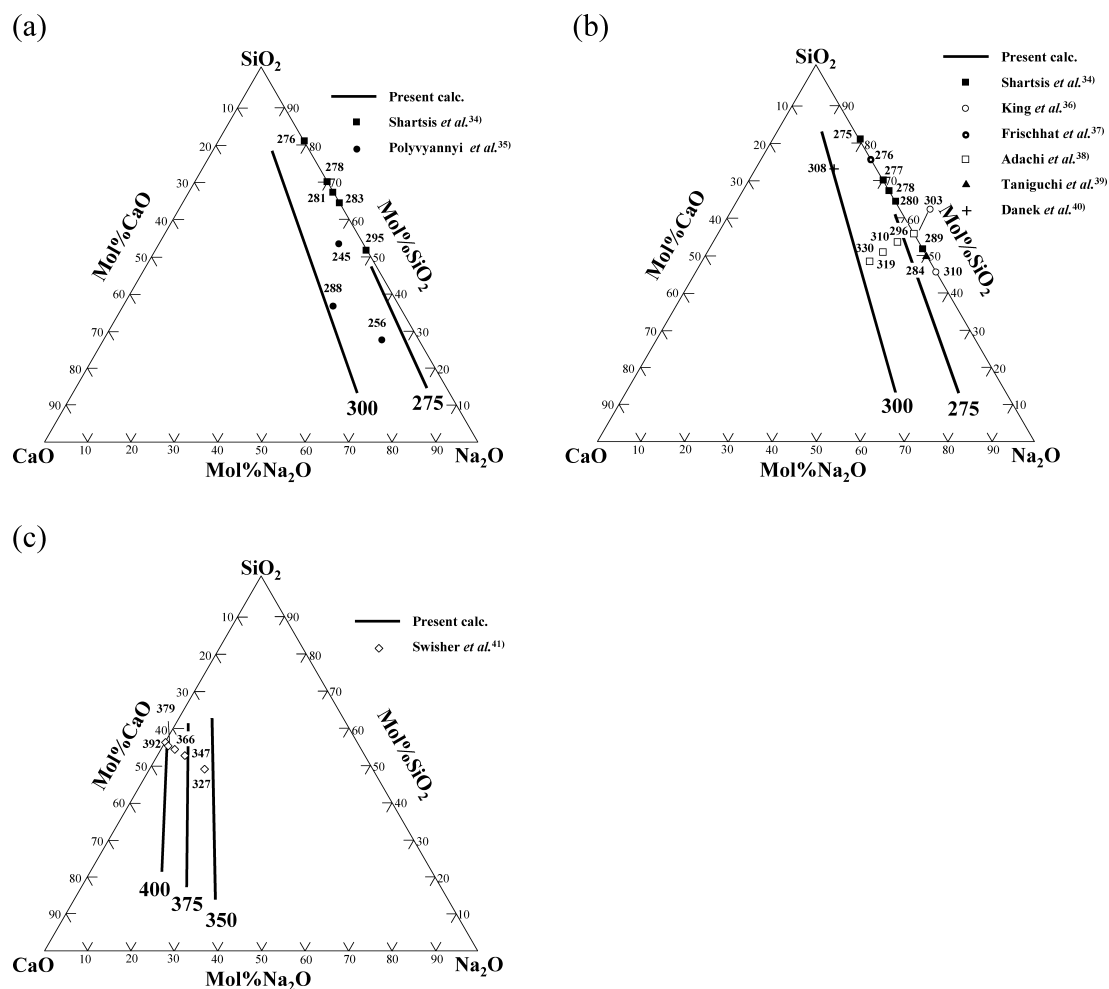


Fig. 4. Surface tension of molten  $\text{SiO}_2$ - $\text{CaO}$ - $\text{Na}_2\text{O}$  system at (a) 1473, (b) 1573 and (c) 1863 K.

has a temperature dependency, since like  $\text{B}_2\text{O}_3$ , the network structures of  $\text{SiO}_2$  consist of tetrahedral  $\text{SiO}_4^{4-}$  ions. However, it is considered that this temperature dependency is much less than that of  $\text{B}_2\text{O}_3$ , because the calculated results are in good agreement with the literature values of several ternary silicates without  $\text{B}_2\text{O}_3$  over a wide temperature range.<sup>14)</sup>

**Figure 3** is a comparison of the surface tension results obtained from the current model and from the experimental data obtained using the  $\text{SiO}_2$ - $\text{CaO}$ - $\text{CaF}_2$  system at 1773 K.<sup>42-47)</sup> The iso-surface tension curves calculated using the current model reproduce the composition dependence of surface tension for this slag, and show that its surface tension increases with increasing  $\text{CaO}$  content.<sup>48)</sup> The calculated results for the  $\text{SiO}_2$ - $\text{CaO}$ - $\text{Na}_2\text{O}$  system at 1473, 1573 and 1863 K are shown in **Fig. 4**. These results are in good agreement with the literature values at each temperature, although the composition region targeted in the present calculation is very narrow. **Figures 5** and **6** show the surface tensions of molten silicates containing  $\text{B}_2\text{O}_3$ . These systems are  $\text{SiO}_2$ - $\text{CaO}$ - $\text{B}_2\text{O}_3$  at 1373, 1573 and 1823 K for Fig. 5, and  $\text{SiO}_2$ - $\text{B}_2\text{O}_3$ - $\text{Na}_2\text{O}$  at 873 and 1173 K for Fig. 6. In these figures, not only the calculated results for  $R_{\text{B}^{3+}}/R_{\text{BO}_3^{3-}} = -0.113 + 1.63 \cdot 10^{-4} T$  but also those for  $R_{\text{B}^{3+}}/R_{\text{O}^{2-}} = 0.1642$  are compared with the experimental data.<sup>16,18)</sup> The  $R_{\text{B}^{3+}}/R_{\text{O}^{2-}} = 0.1642$  represents that the existence of  $\text{BO}_3^{3-}$  units is ignored in the  $\text{B}_2\text{O}_3$  melts. The calculated results

for  $R_{\text{B}^{3+}}/R_{\text{BO}_3^{3-}} = -0.113 + 1.63 \cdot 10^{-4} T$  and  $R_{\text{B}^{3+}}/R_{\text{O}^{2-}} = 0.1642$  are drawn as solid lines and dashed lines in these figures, respectively. There is only a slight difference between the iso-surface tension curves of  $R_{\text{B}^{3+}}/R_{\text{BO}_3^{3-}} = -0.113 + 1.63 \cdot 10^{-4} T$ , and those of the  $R_{\text{B}^{3+}}/R_{\text{O}^{2-}} = 0.1642$  in  $\text{SiO}_2$ - $\text{CaO}$ - $\text{B}_2\text{O}_3$  systems in Figs. 5(b) and 5(c), because both ratios have similar values as shown in Fig. 2. These curves reproduce the experimental values<sup>16)</sup> at these temperatures. At 1373 in Fig. 5(a), however, the results calculated for  $R_{\text{B}^{3+}}/R_{\text{BO}_3^{3-}} = -0.113 + 1.63 \cdot 10^{-4} T$  agree better with the literature data rather than those for  $R_{\text{B}^{3+}}/R_{\text{O}^{2-}} = 0.1642$ . In Fig. 6 the calculated results of  $R_{\text{B}^{3+}}/R_{\text{O}^{2-}} = 0.1642$  for the molten silicates containing two surface-active components ( $\text{B}_2\text{O}_3$  and  $\text{Na}_2\text{O}$ ) deviate greatly from the measured values.<sup>18)</sup> On the other hand, the surface tensions calculated for  $R_{\text{B}^{3+}}/R_{\text{BO}_3^{3-}} = -0.113 + 1.63 \cdot 10^{-4} T$  show good agreement with the surface tensions in the  $\text{SiO}_2$ - $\text{B}_2\text{O}_3$ - $\text{Na}_2\text{O}$  system at both temperatures. The average error assessed using Eq. (6) was 4.5% in all systems of the present work, which means the surface tensions in systems containing surface-active components are well predicted using the current model.

The above results indicate the following: by considering the ionic radii of the components in melts, the current model is applicable to the surface tension evaluations of ternary molten silicates containing surface-active constituents, such as  $\text{B}_2\text{O}_3$ ,  $\text{CaF}_2$  or  $\text{Na}_2\text{O}$ . Especially, the cur-

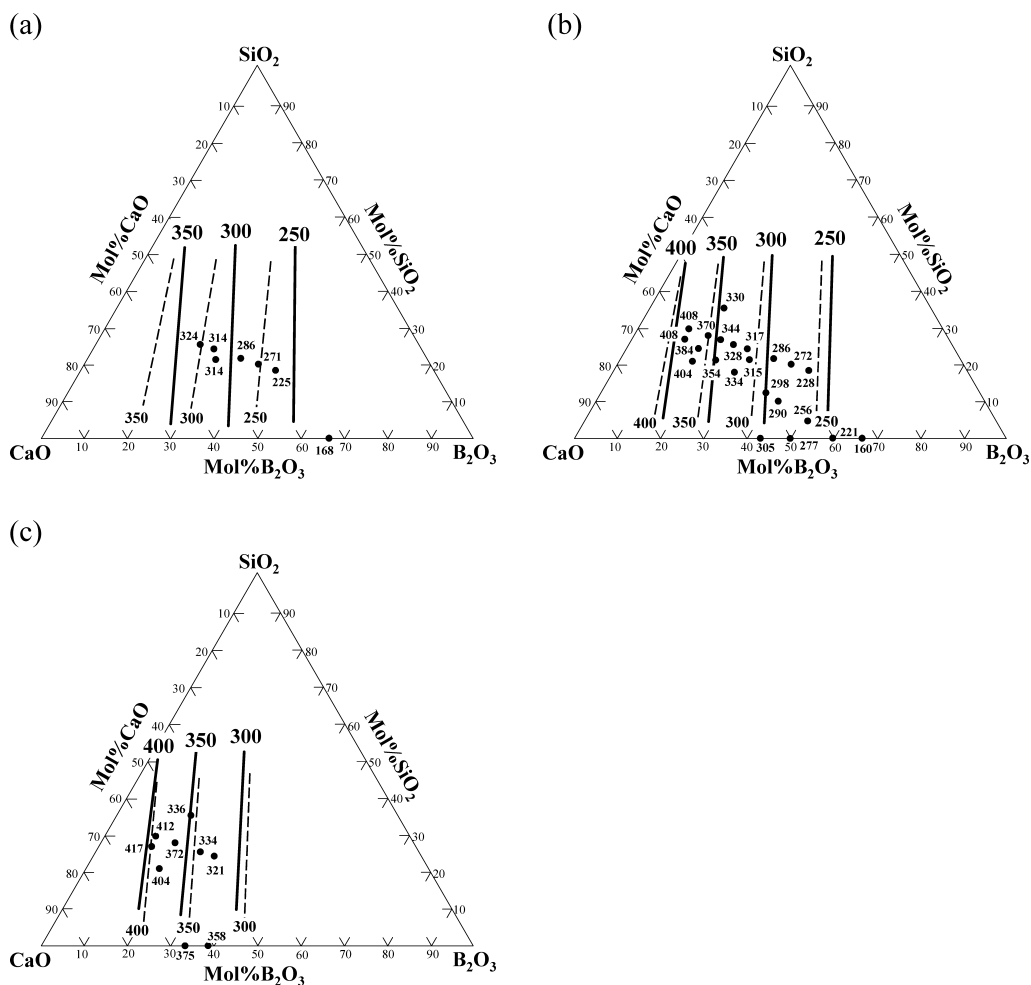


Fig. 5. Surface tension of molten  $\text{SiO}_2$ - $\text{CaO}$ - $\text{B}_2\text{O}_3$  system at (a) 1373, (b) 1573 and (c) 1823. Solid line: present calc. for  $R_{\text{B}^{3+}}/R_{\text{BO}_3^-} = -0.113 + 1.63 \cdot 10^{-4} T$ . Dashed line: present calc. for  $R_{\text{B}^{3+}}/R_{\text{O}^{2-}} = 0.1642$ . Closed circle: Walker *et al.*<sup>16)</sup>

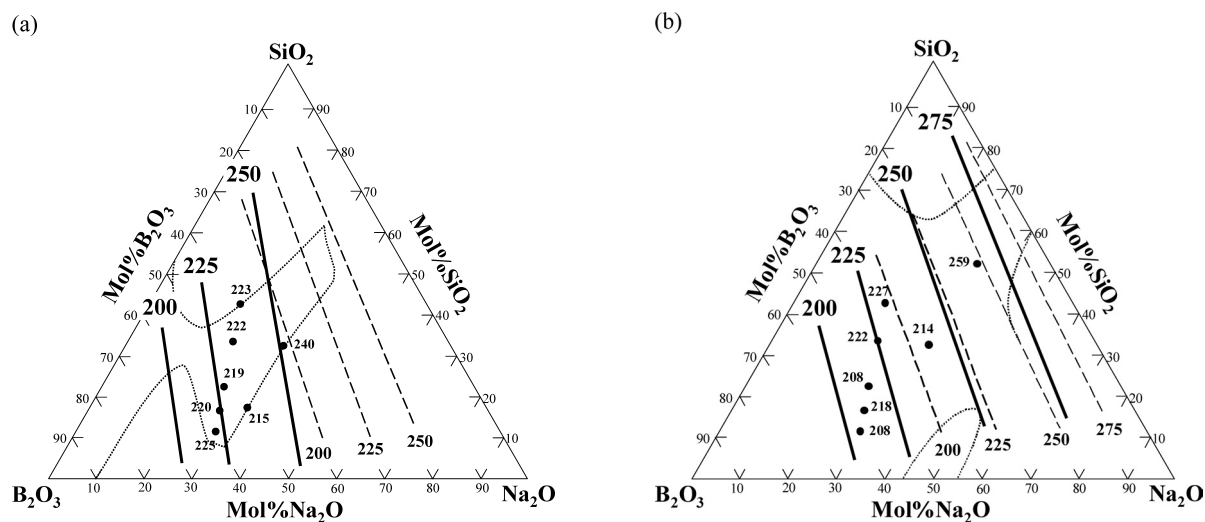


Fig. 6. Surface tension of molten  $\text{SiO}_2$ - $\text{B}_2\text{O}_3$ - $\text{Na}_2\text{O}$  system at (a) 973 and (b) 1173 K. Solid line: present calc. for  $R_{\text{B}^{3+}}/R_{\text{BO}_3^-} = -0.113 + 1.63 \cdot 10^{-4} T$ . Dashed line: present calc. for  $R_{\text{B}^{3+}}/R_{\text{O}^{2-}} = 0.1642$ . Closed circle: Ahari *et al.*<sup>18)</sup> Dotted line: liquidus.<sup>49)</sup>

rent model reproduces the surface tensions for systems containing  $\text{B}_2\text{O}_3$  over a wide temperature range (from 873 to 1823 K) by taking into account the existence of  $\text{BO}_3^{3-}$  units in the melts.

#### 4. Conclusions

A thermodynamic model for evaluating the surface tension of molten silicates by considering the ionic radii of



their constituents was applied to the silicate melts containing the following surface-active components:  $B_2O_3$ ,  $CaF_2$  or  $Na_2O$ . The results from the present model agreed with the literature values in these ternary systems.

# REFERENCES

- 1) M. Kawamoto, T. Kanazawa, S. Hiraki and S. Kumakura: Proc. of the 5th Int. Conf. on Molten Slags, Fluxes and Salts, the Iron & Steel Society, Warrendale, PA, (1997), 777.
- 2) K. C. Mills, A. B. Fox, R. P. Thackray and Z. Li: Proc. of VII Int. Conf. on Molten Slags, Fluxes and Salts, the South African Institute of Mining and Metallurgy, Johannesburg, (2004), 713.
- 3) J. van der Schaaf and R. G. C. Beerkens: *J. Colloid Interface Sci.*, **295** (2006), 218.
- 4) K. C. Mills and B. J. Keene: *Int. Mater. Rev.*, **32** (1987), 1.
- 5) K. Nakajima: *Tetsu-to-Hagane*, **80** (1994), 599.
- 6) R. E. Boni and G. Derge: *J. Met.*, **206** (1956), 53.
- 7) T. Tanaka, K. Hack, T. Iida and S. Hara: *Z. Metallkd.*, **87** (1996), 380.
- 8) T. Tanaka, S. Hara, M. Ogawa and T. Ueda: *Z. Metallkd.*, **89** (1998), 368.
- 9) T. Ueda, T. Tanaka and S. Hara: *Z. Metallkd.*, **90** (1999), 342.
- 10) T. Tanaka and S. Hara: *Z. Metallkd.*, **90** (1999), 348.
- 11) T. Tanaka, M. Nakamoto and T. Usui: Proc. of Japan-Korea Workshop on Science and Technology in Ironmaking and Steelmaking, The Iron and Steel Institute of Japan, Tokyo, (2003), 56.
- 12) J. A. V. Butler: *Proc. R. Soc. A*, **135** (1932), 348.
- 13) T. Tanaka, T. Kitamura and I. A. Back: *ISIJ Int.*, **46** (2006), 400.
- 14) M. Nakamoto, A. Kiyose, T. Tanaka, L. Holappa and M. Hämäläinen: *ISIJ Int.*, **47** (2007), 38.
- 15) H. Scholze: *Glas; Natur, Struktur und Eigenschaften*, Springer-Verlag, Berlin, (1977), 265.
- 16) R. D. Walker and T. A. T. Fray: Int. Symp.—Advances in Extractive Metallurgy, Inst. Mining. Metall., London, (1977), 13-19.
- 17) E. T. Turkdogan: Physicochemical Properties of Molten Slags and Glasses, The Metals Society, London, (1983), 77.
- 18) K. Ghanbari-Ahari, K. Askari and A. M. Cameron: *Phys. Chem. Glasses*, **32** (1991), 72.
- 19) H. Maekawa, Y. Inagaki, S. Shimokawa and T. Yokokawa: *J. Chem. Phys.*, **103** (1995), 371.
- 20) N. Iwamoto and Y. Makino: *J. Non-Cryst. Solids*, **46** (1981), 81.
- 21) Y. Tsunawaki, N. Iwamoto, T. Hattori and A. Mitsuishi: *J. Non-Cryst. Solids*, **44** (1981), 369.
- 22) R. W. Luth: *Am. Mineral.*, **73** (1988), 297.
- 23) J. F. Stebbins and Q. Zeng: *J. Non-Cryst. Solids*, **262** (2000), 1.
- 24) M. Mohri, Y. Sasaki and K. Ishii: *ISIJ Int.*, **41** (2001), 410.
- 25) J. H. Park, D. J. Min and H. S. Song: *ISIJ Int.*, **42** (2002), 344.
- 26) T. J. Kiczinski and J. F. Stebbins: *J. Non-Cryst. Solids*, **306** (2002), 160.
- 27) M. Hayashi, N. Nabeshima, H. Fukuyama and K. Nagata: *ISIJ Int.*, **42** (2002), 352.
- 28) Y. Sasaki, M. Mohri and K. Ishii: *ISIJ Int.*, **43** (2003), 1897.
- 29) R. D. Shannon: *Acta Cryst.*, **A32** (1976), 751.
- 30) N. Ikemiya, J. Umemoto, S. Hara and K. Ogino: *ISIJ Int.*, **33** (1993), 156.
- 31) NIST molten Salt Database, National Institute of Standards and Technology, (1987).
- 32) B. J. Keene: *Slag Atlas*, 2nd Ed., Verlag Stahleisen GmbH, Düsseldorf, (1995), 403.
- 33) X. Chen, S. Jingui, S. Nishimura, Y. Oyama and K. Terashima: *J. Cryst. Growth*, **240** (2002), 445.
- 34) L. Shartsis and S. Spinner: *J. Res. NBS*, **46** (1951), 385.
- 35) I. P. Polyvannyi, V. A. Lata, A. A. Adilova and L. P. Ibakina: *Viniti (USSR)*, Rept. No. 3782-80 (1980).
- 36) T. B. King: *Glass Technol.*, **35** (1951), 241.
- 37) G. H. Frischhat and W. Beier: *Glastech. Ber.*, **52** (1979), 116.
- 38) A. Adachi, K. Ogino and H. Toritani: *Technol. Rep. Osaka Univ.*, **10** (1960), 149.
- 39) H. Taniguchi: *Contrib. Mineral. Petrol.*, **100** (1988), 484.
- 40) V. Danek and T. Licko: *Silikaty*, **25** (1981), 153.
- 41) J. H. Swisher and C. L. McCabe: *Trans. Metall. Soc. AIME*, **230** (1964), 1669.
- 42) S. B. Yakobashvili and I. I. Frumin: *Autom. Weld. (USSR)*, **15** (1962), 33.
- 43) S. M. Pupynina, S. E. Volkov, O. S. Bobkova and V. S. Petukhov: *Sb. Tr. Tsentr. Inst. Chernaya Metal.*, **70** (1967), 47.
- 44) S. M. Pupynina and S. E. Volkov: *Teoriya Metallurgicheskikh Protessov*, Metallurgizdat, Moscow, (1971), 156.
- 45) A. Ejima and M. Shimoji: *Trans. Faraday Soc.*, **66** (1970), 99.
- 46) Yu. P. Nikitin and A. N. Safonnikov: *Sb. Nauchni Tr. Uralsk. Politekh. Inst.*, **126** (1963), 68.
- 47) Yu. M. Gogiberidze, T. I. Dzinchardze and Sh. M. Mikiashvili: *Soobshcheniya Akad. Nauk Gruz. SSR*, **3** (1968), 695.
- 48) K. C. Mills and B. J. Keene: *Int. Met. Rev.*, **26** (1981), 21.
- 49) *Phase Diagrams for Ceramists*, ed. by M. K. Reser, The American Ceramic Society, Ohio, (1964), 184.