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

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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.^{1,2)} 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 .²⁾ 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.³⁾

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.^{4,5)} Mills and Keene⁴⁾ 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^{4–6)} have been developed for evaluating the surface tension of molten slag containing surface-active components. Mills and Keene⁴⁾ modified Boni and Derge's model⁶⁾ 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. Nakajima⁵⁾ 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.*^{7–11)} 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.¹²⁾ 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.*¹³⁾ 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 SiO_2 , Al_2O_3 , CaO , FeO , MgO or MnO .¹⁴⁾ 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, B_2O_3 , CaF_2 or Na_2O .

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

The Eqs. (1), (2) and (3) for evaluating the surface tension (σ) of the AX–BY–CZ melts have been derived from Butler's equation¹²⁾ by considering the assumptions [1] and [2].^{13,14)}

[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. σ_i^{Pure} is the surface tension of pure molten compound i ($i = \text{AX}, \text{BY}$ or 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^{P} is the mole fraction of compound i in phase P ($\text{P} = \text{Surf}$ or Bulk). 'Surf' and 'Bulk' indicate the surface and the bulk, respectively. R_{A} , R_{B} and R_{C} correspond to the

radii of cations A, B and C, while R_{X} , R_{Y} and R_{Z} correspond to the radii of anions X, Y and Z. For example, in the case of the SiO_2 – CaO – 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 SiO_4^{4-} is considered to be the minimum anionic unit in 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^{13,14)} was used in this study. Here, B_2O_3 glass melts are considered to be constructed from BO_3^{3-} units.^{15–19)} Therefore, we must assume that the ratio of cationic to anionic radii for B_2O_3 is $R_{\text{B}^{3+}}/R_{\text{BO}_3^{3-}}$, and treat it as a parameter in this model, as well as in 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 CaF_2 since it is generally recognized that F^- in the silicate melts is not coordinated to Si^{4+} , which means that CaF_2 is merely dissociated in the molten silicate. This was stated experimentally by several researchers.^{20–28)} The ionic radii data were extracted from the database compiled by Shannon,²⁹⁾ while the molar volumes of the pure oxides (except B_2O_3), as recommended by Mills and Keene,⁴⁾ were used in the present calculations. The equation to determine the temperature dependence for the molar volume of pure B_2O_3 was considered on the basis of the B_2O_3 melting point³⁰⁾ and the recommended temperature dependence of molar volume (0.01%/K).⁴⁾ 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 SiO_2 , B_2O_3 and CaF_2 , as suggested by NIST,³¹⁾ were used for the calculations in this study, since there is a large volume of surface tension measurements for these components.^{32,33)} Due to a lack of surface tension data for pure

Table 1. Cationic and anionic radii (Å).²⁹⁾

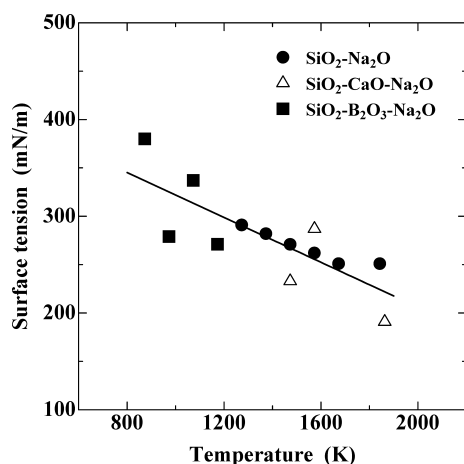
Si^{4+}	0.42
B^{3+}	0.23
Ca^{2+}	0.99
Na^+	0.97
F^-	1.33
O^{2-}	1.44

Table 2. Molar volume of pure component (m^3/mol).^{4,30)}

Oxide	Temperature (K) dependence of molar volume (m^3/mol)
SiO_2	$27.516 \{ 1 + 1 \cdot 10^{-4} (T - 1773) \} \cdot 10^{-6}$
B_2O_3	$45.8 \{ 1 + 1 \cdot 10^{-4} (T - 723) \} \cdot 10^{-6}$
CaF_2	$31.3 \{ 1 + 1 \cdot 10^{-4} (T - 1773) \} \cdot 10^{-6}$
CaO	$20.7 \{ 1 + 1 \cdot 10^{-4} (T - 1773) \} \cdot 10^{-6}$
Na_2O	$33.0 \{ 1 + 1 \cdot 10^{-4} (T - 1773) \} \cdot 10^{-6}$

Table 3. Model parameters (temperature dependences of surface tension for pure oxides).* NIST,³¹⁾ ** previous work¹⁴⁾ and *** present work.

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

**Fig. 1.** Evaluated surface tension of pure Na₂O.

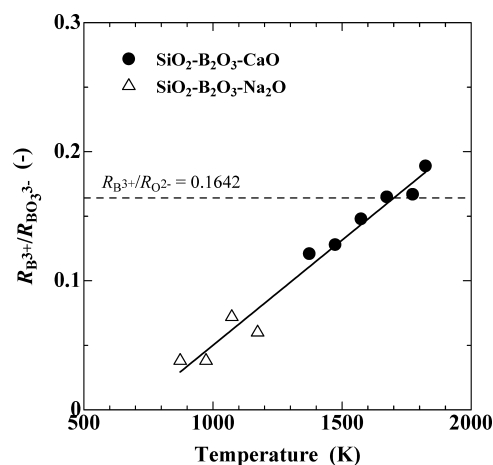
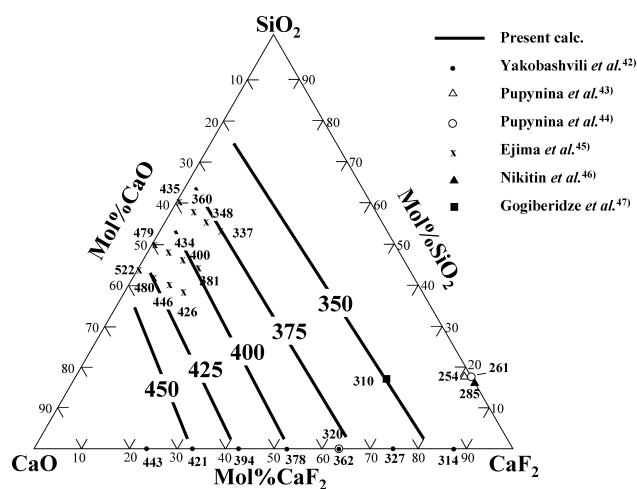
Na₂O, the temperature dependent surface tension of this component was evaluated from the literature values for the binary and ternary systems containing Na₂O.^{6,18,32,34-41)} For this purpose, the following systems and temperatures were selected:

- SiO₂-Na₂O at 1273, 1373, 1473, 1573, 1673 and 1843 K
- SiO₂-CaO-Na₂O at 1473, 1573 and 1863 K
- SiO₂-B₂O₃-Na₂O at 873, 973, 1073 and 1173 K

The temperature dependent surface tension for pure CaO evaluated in the previous work¹⁴⁾ 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 B₂O₃ ($R_{B^{3+}}/R_{BO_3^{3-}}$) have been assessed in the present model. Therefore, the surface tensions for pure Na₂O and $R_{B^{3+}}/R_{BO_3^{3-}}$ were determined simultaneously by fitting the calculated values to the experimental values only in the SiO₂-B₂O₃-Na₂O system.¹⁸⁾ The SiO₂-CaO-B₂O₃ system at 1373, 1473, 1573, 1673, 1773 and 1823 K¹⁶⁾ was also used for determining $R_{B^{3+}}/R_{BO_3^{3-}}$.

The surface tensions for pure Na₂O, obtained from the evaluations in the silicate systems containing Na₂O, are plotted in **Fig. 1**. These surface tensions were obtained by minimizing the average error between the calculated results and literature values,^{6,18,32,34-41)} 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 SiO₂-CaO-CaF₂ system at 1773 K.

σ_{Expe} and σ_{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 Na₂O. **Figure 2** shows the relation between the temperature and $R_{B^{3+}}/R_{BO_3^{3-}}$ from the evaluations of the SiO₂-B₂O₃-Na₂O and SiO₂-CaO-B₂O₃ systems. From this figure, it is found that $R_{B^{3+}}/R_{BO_3^{3-}}$ is dependent on temperature. Scholze¹⁵⁾ 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 B₂O₃. On the basis of investigations by nuclear magnetic resonance, Maekawa *et al.*¹⁹⁾ reported that the connectivity of BO_3^{3-} units in the structure of molten B₂O₃ has a certain temperature dependency. Although there is no exact knowledge about the structural change at the surface of B₂O₃ melts with increasing temperature, it is considered that the results of $R_{B^{3+}}/R_{BO_3^{3-}}$ reflect the temperature dependence of the B₂O₃ 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 SiO₂ also

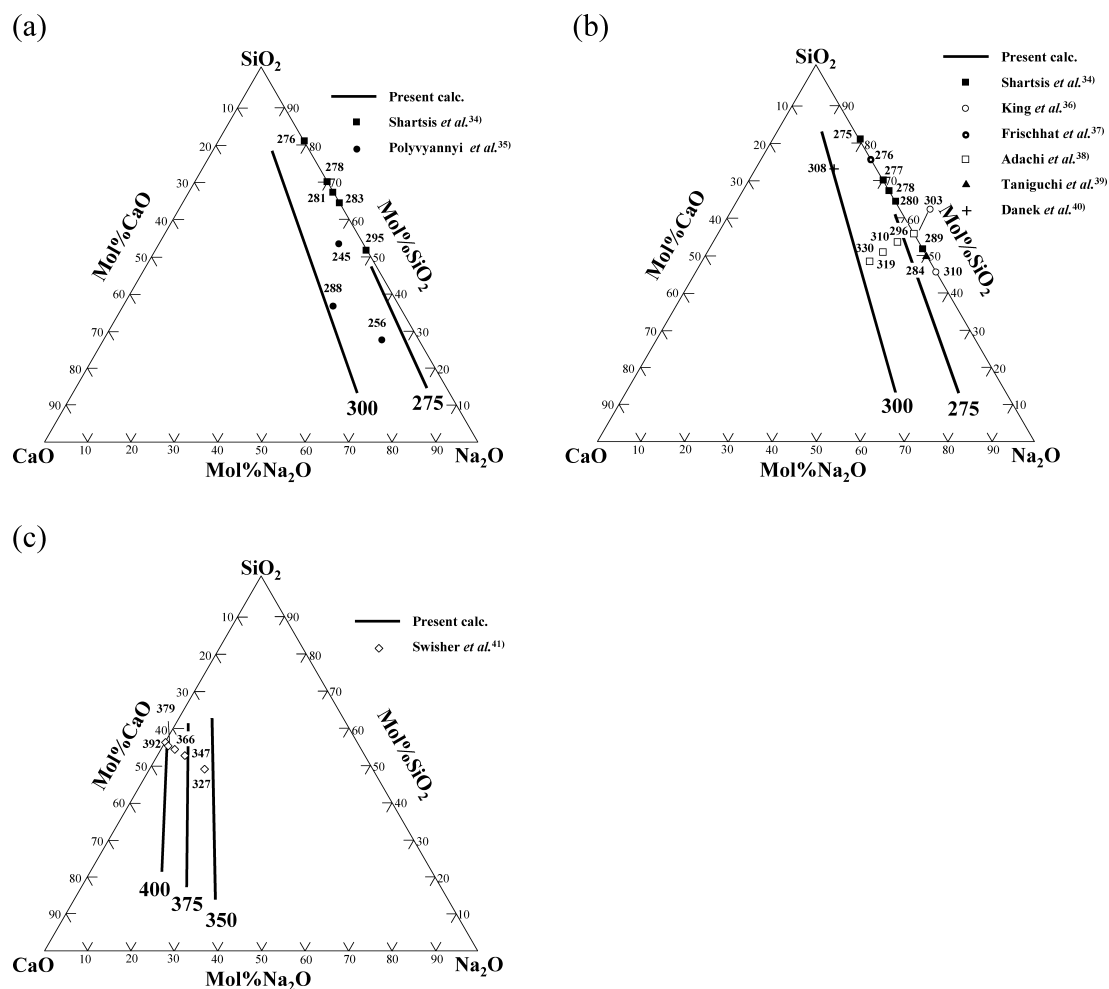


Fig. 4. Surface tension of molten SiO_2 -CaO- Na_2O system at (a) 1473, (b) 1573 and (c) 1863 K.

has a temperature dependency, since like B_2O_3 , the network structures of SiO_2 consist of tetrahedral SiO_4^{4-} ions. However, it is considered that this temperature dependency is much less than that of B_2O_3 , because the calculated results are in good agreement with the literature values of several ternary silicates without B_2O_3 over a wide temperature range.¹⁴⁾

Figure 3 is a comparison of the surface tension results obtained from the current model and from the experimental data obtained using the SiO_2 -CaO- CaF_2 system at 1773 K.⁴²⁻⁴⁷⁾ 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 CaO content.⁴⁸⁾ The calculated results for the SiO_2 -CaO- Na_2O 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 B_2O_3 . These systems are SiO_2 -CaO- B_2O_3 at 1373, 1573 and 1823 K for Fig. 5, and SiO_2 - B_2O_3 - Na_2O 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.^{16,18)} The $R_{\text{B}^{3+}}/R_{\text{O}^{2-}} = 0.1642$ represents that the existence of BO_3^{3-} units is ignored in the B_2O_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 SiO_2 -CaO- B_2O_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 values¹⁶⁾ 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 (B_2O_3 and Na_2O) deviate greatly from the measured values.¹⁸⁾ 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 SiO_2 - B_2O_3 - Na_2O 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 B_2O_3 , CaF_2 or Na_2O . Especially, the cur-

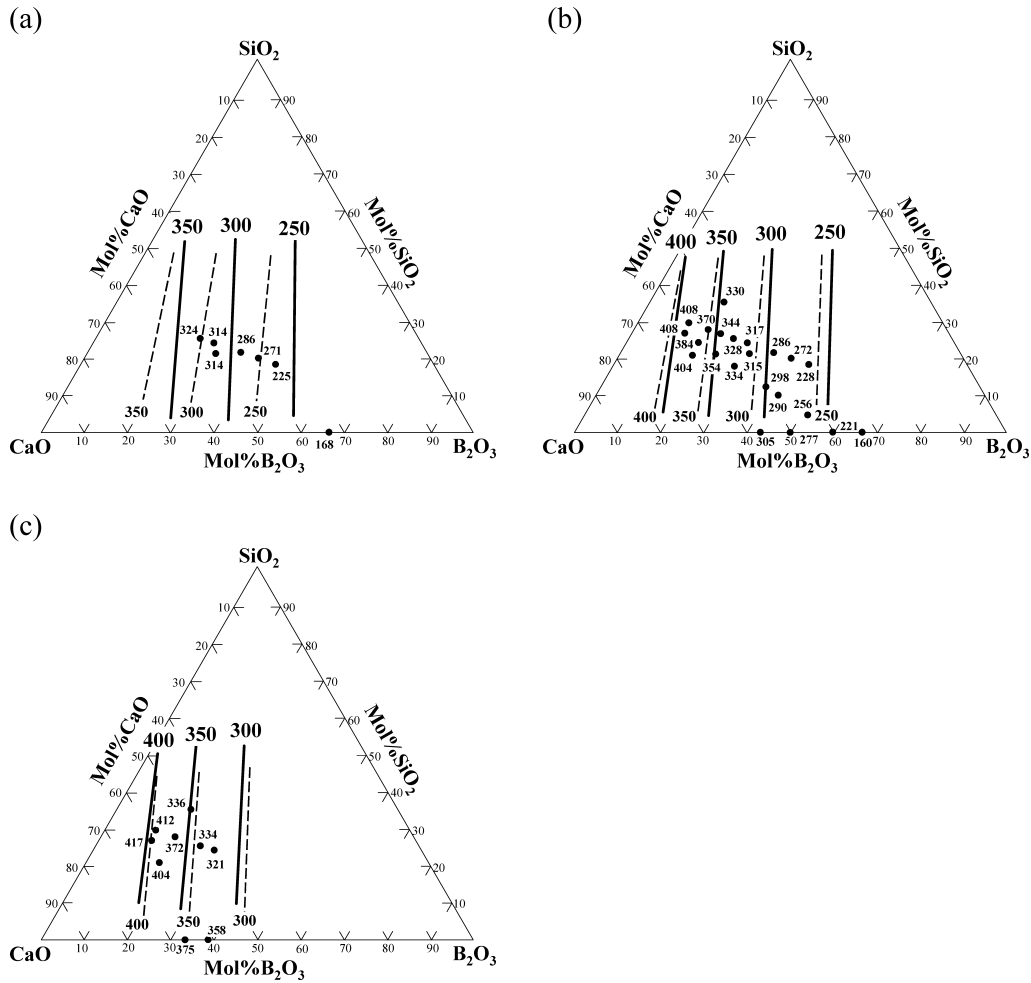


Fig. 5. Surface tension of molten SiO_2 - CaO - B_2O_3 system at (a) 1373, (b) 1573 and (c) 1823. Solid line: present calc. for $R_{\text{B}^{3+}}/R_{\text{BO}_3^-} = -0.113 + 1.63 \cdot 10^{-4} T$. Dashed line: present calc. for $R_{\text{B}^{3+}}/R_{\text{O}^{2-}} = 0.1642$. Closed circle: Walker *et al.*¹⁶⁾

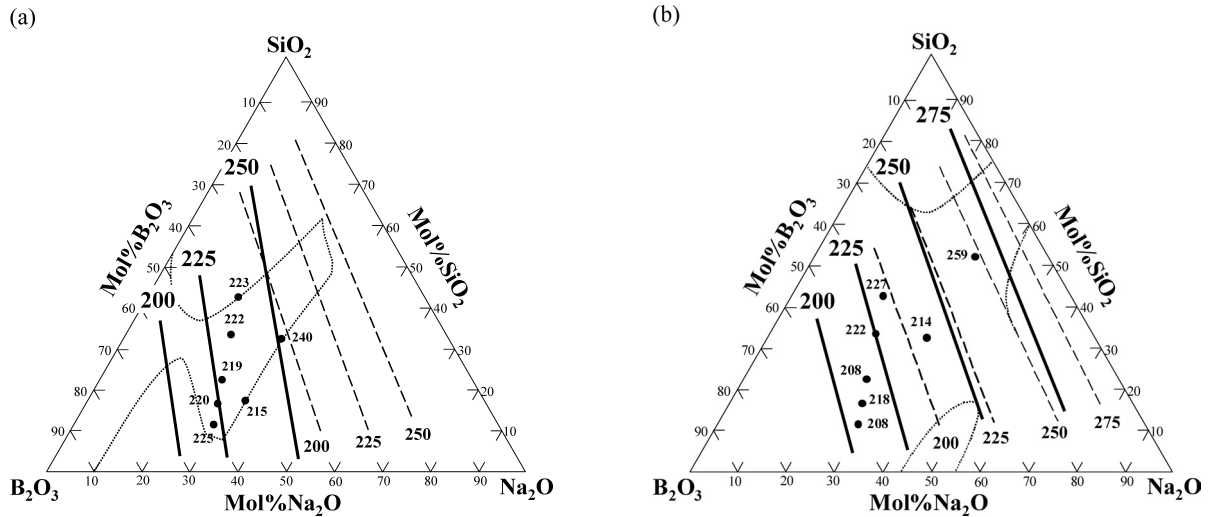


Fig. 6. Surface tension of molten SiO_2 - B_2O_3 - Na_2O system at (a) 973 and (b) 1173 K. Solid line: present calc. for $R_{\text{B}^{3+}}/R_{\text{BO}_3^-} = -0.113 + 1.63 \cdot 10^{-4} T$. Dashed line: present calc. for $R_{\text{B}^{3+}}/R_{\text{O}^{2-}} = 0.1642$. Closed circle: Ahari *et al.*¹⁸⁾ Dotted line: liquidus.⁴⁹⁾

rent model reproduces the surface tensions for systems containing B_2O_3 over a wide temperature range (from 873 to 1823 K) by taking into account the existence of 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.

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