Evaluation of Surface Tension of Molten Ionic Mixtures

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A thermodynamic model was derived to evaluate the surface tension of molten ionic mixtures by considering the ratio of the radius of cation to that of anion. The present model reproduces the following characteristics of the composition dependence of surface tension in molten alkaline–halide ionic mixtures precisely.
- almost linear change with the composition in common cation systems:
- large concave feature of the composition dependence in common anion systems.

The present model can be applied to evaluate the surface tension molten ionic mixtures with complex anion such as sulfate as well as molten SiO_2 based binary systems considering effective ionic radii for complex anions.

KEY WORDS: surface tension; thermodynamics; molten slag; SiO_2; ionic radius.

1. Introduction

Since surface tension of molten ionic mixtures such as molten slag is an important physico-chemical properties directly related to various surface phenomena in steelmaking processes, e.g. wettability with liquid steel and refractories, etc., there have been accumulated a lot of data so far. The authors have developed a system to evaluate various physico-chemical properties such as surface tension and viscosity on the basis of thermodynamic databases,[1–4] which are usually used to calculate phase equilibria, chemical reactions etc. The simultaneous evaluation of those various properties is quite significant to investigate complicated phenomena at high temperature in steelmaking processes. Recently we could evaluate phase diagrams in nano-sized alloys from the above evaluation system[1,5,6] by considering simultaneously both of phase equilibria and the surface properties. At the present stage, we can evaluate the surface tension of liquid alloys[1–6] by using Butler's equation[7] with a procedure proposed by Speiser et al.[8,9] On the other hand, we can not apply these procedures to evaluate the surface tension of molten ionic mixtures and molten slag, and we have had still some problems[2,4,10–13] on the evaluation of the surface tension even for molten alkaline–halide binary mixtures, which are the simplest group in molten ionic mixtures.

In the present paper, we discuss those problems on the evaluation of the surface tension of molten ionic mixtures, and then we propose a new model to evaluate the surface tension of those ionic mixtures and molten SiO_2 based binary systems.

2. Evaluation of Surface Tension of Liquid Alloys

First of all, the evaluation of the surface tension σ of liquid alloys[1–6] is discussed in this section in order to make clear some problems on the surface tension of molten ionic mixtures described later. Here, we use the following Eqs. (1) and (2) to evaluate the surface tension of liquid alloys. These equations were derived[14] by one of the authors to re-invesitigate the derivation of Butler's model.[7] The formula is the same as that derived by Butler.[7]

$$\sigma = \sigma_A^{Pure} + \frac{RT}{A_A} \ln \frac{N_A^{Surf}}{N_A^{Bulk}}$$

$$+ \frac{1}{A_A} \{G_A^{E,Surf}(T, N_B^{Surf}) - G_A^{E,Bulk}(T, N_B^{Bulk})\} \quad ....(1)$$

$$\sigma = \sigma_B^{Pure} + \frac{RT}{A_B} \ln \frac{N_B^{Surf}}{N_B^{Bulk}}$$

$$+ \frac{1}{A_B} \{G_B^{E,Surf}(T, N_B^{Surf}) - G_B^{E,Bulk}(T, N_B^{Bulk})\} \quad ....(2)$$

In Eqs. (1) and (2), σ_i^{Prure} is the surface tension of pure component i, $A_i = L N_0^{1/3} V_i^{2/3}$ (N_0: Avogadro's number, $L=1.091$ for liquid metals, V_i: molar volume of pure component i) is the molar surface area of pure component i. Superscripts Bulk and Surf show bulk and surface, respectively. Here the surface is assumed to be an outermost monolayer of a material. N_i^P is mole fraction of component i in the bulk ($P=$Bulk) and the surface ($P=$Surf). $G_i^{E,P}(T, N_B^P)$ is partial excess Gibbs energy of component i in the bulk ($P=$Bulk) and the surface ($P=$Surf), which is a function of temperature T and the mole fraction of component B
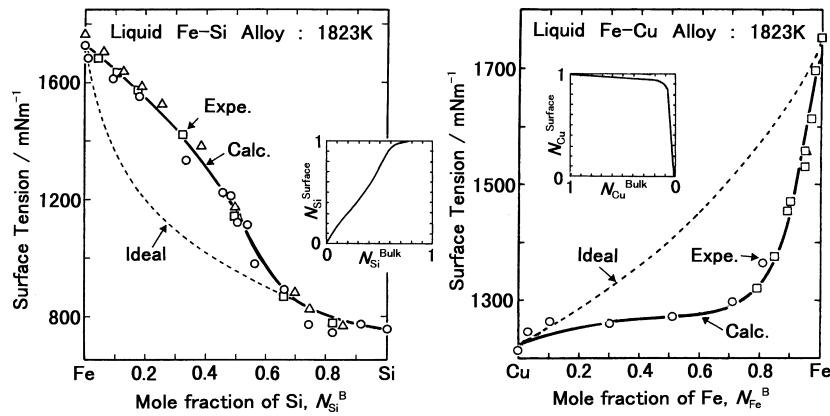
Fig. 1. Surface tension of liquid binary alloys. Calc. from Eqs. (1), (2), (3) and (4): solid curves, Expe. in Fe–Si: △ (Ref. 17), ○ (Ref. 16), □ (Ref. 18), Expe. in Fe–Cu: ○ (Ref. 19), □ (Ref. 20).

N_B. In Eqs. (1) and (2), $G_i^{E,Bulk}(T, N_B^{Bulk})$ in the bulk can be obtained directly from thermodynamic databases, but $G_i^{E,Surf}(T, N_B^{Surf})$ for the surface can be estimated from the following approximation proposed by Speiser *et al.*[8,9]

$$G_i^{E,Surf}(T, N_B^{Surf}) = \beta^{MIX} \cdot G_i^{E,Bulk}(T, N_B^{Surf}) \dots \dots (3)$$

The above equation means that the excess Gibbs energy in the surface has the same function of temperature and composition as that in the bulk, but the mole fraction is replaced by $N_B^{Surface}$. β^{MIX} is a parameter related to the ratio of the coordination number in the surface to that in the bulk Z^{Surf}/Z^{Bulk}. For example, Speiser *et al.*[8,9] proposed $\beta^{MIX} = Z^{Surf}/Z^{Bulk} = 9/12 = 0.75$ by assuming a closed packed solid structure. However, since the value β^{MIX} for liquid can not be evaluated exactly, the authors determined the apparent ratio of $(Z^{Surf})'/Z^{Bulk}$ for liquid metals and alloys from the relationship between the surface tension of pure metals and the binding energy per unit area[1–6,10–13]:

$$\beta^{MIX} = \frac{(Z^{Surf})'}{Z^{Bulk}} = 0.83 \quad : \quad \text{for pure metals and alloys} \dots (4)$$

The procedure to calculate the surface tension of liquid alloys σ in Eqs. (1) and (2) is as follows[1–6]:

(1) The surface tensions, the molar volumes of pure components and excess Gibbs energies in the bulk of components A and B are substituted in Eqs. (1) and (2) at a given temperature and composition.

(2) Equations (1) and (2) are the equations having two unknowns; the surface tension of liquid alloys σ and the surface composition $N_B^{Surface}$.

(3) These equations are solved numerically to determine σ and $N_B^{Surface}$.

As shown in **Fig. 1**, the calculated results[2,4,15] of the surface tension of liquid alloys (solid curves) in Fe–Si and Fe–Cu systems agree well with the experimental values.[16–20] The relationship between N_B^{Bulk} and $N_B^{Surface}$ are indicated in small squares in Fig. 1. It was found from Fig. 1 that when alloys have negative excess Gibbs energy, *e.g.* Fe–Si alloy, the surface tension deviates positively from the surface tension in ideal solution. On the other hand, when alloys have positive excess Gibbs energy, *e.g.* Fe–Cu alloy, the surface tension deviates negatively from that in ideal solution.[2–4] These thermodynamic characteristics can be generally ap-
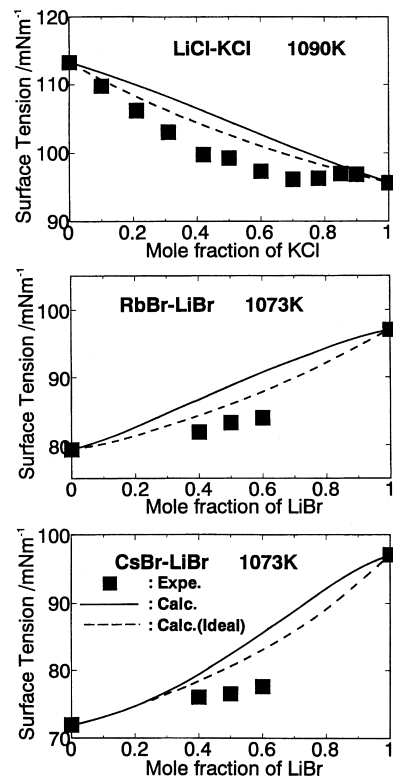

Fig. 2. Surface tension of molten ionic mixtures. Calc. from Eqs. (1), (2) and (3) with $\beta^{MIX} = 0.94$: solid curves, ■: Expe. (Ref. 21).

plied to liquid alloys.[1–6]

3. Problems in Evaluation of Surface Tension of Molten Ionic Mixtures

By applying the above procedure for liquid alloys, we tried to evaluate the surface tension of molten ionic mixtures.[10–13] Some of the results[10] are shown as solid curves in **Fig. 2** although we used $\beta^{MIX} = (Z^{Surf})'/Z^{Bulk} = 0.94$, which had been obtained for ionic mixtures[10–13] by applying the same procedure to determine the above Eq. (4). As can be seen in Fig. 2, the calculated results (solid curves)[10–13] do not agree with the experimental values (■).[21] Especially, although those molten ionic mixtures have negative excess Gibbs energies, the experimental values of the surface ten-

sion deviate negatively from that in the ideal solution,[10] which do not obey the above thermodynamic characteristics of the composition dependence of the surface tension in liquid alloys. In other words, the calculated results exist at the opposite sides against the surface tension of ideal solutions, which means that we can not evaluate the surface tension of

molten ionic mixtures by considering only the ratio of the coordination number in the surface to that in the bulk.[10–13] Then, we proposed the following equation to evaluate the value of β^{MIX} to cope with the above problems in our previous work[10–13]:

Fig. 3(a). Surface tension of molten ionic mixtures in commom cation alkaline–halide systems. Dotted curve: from Eqs. (1), (2) and (4); solid curves: from Eqs. (6) and (7). ■: Expe. (Ref. 21).
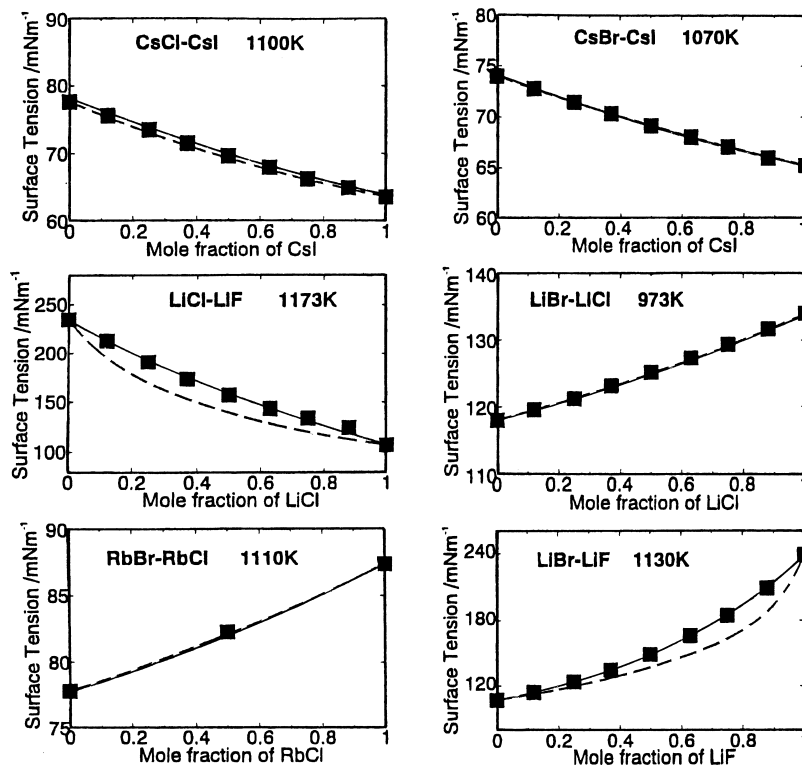

Fig. 3(b). Surface tension of molten ionic mixtures in commom cation alkaline–halide systems. Dotted curve: from Eqs. (1), (2) and (4); solid curves: from Eqs. (6) and (7). ■: Expe. (Ref. 21).
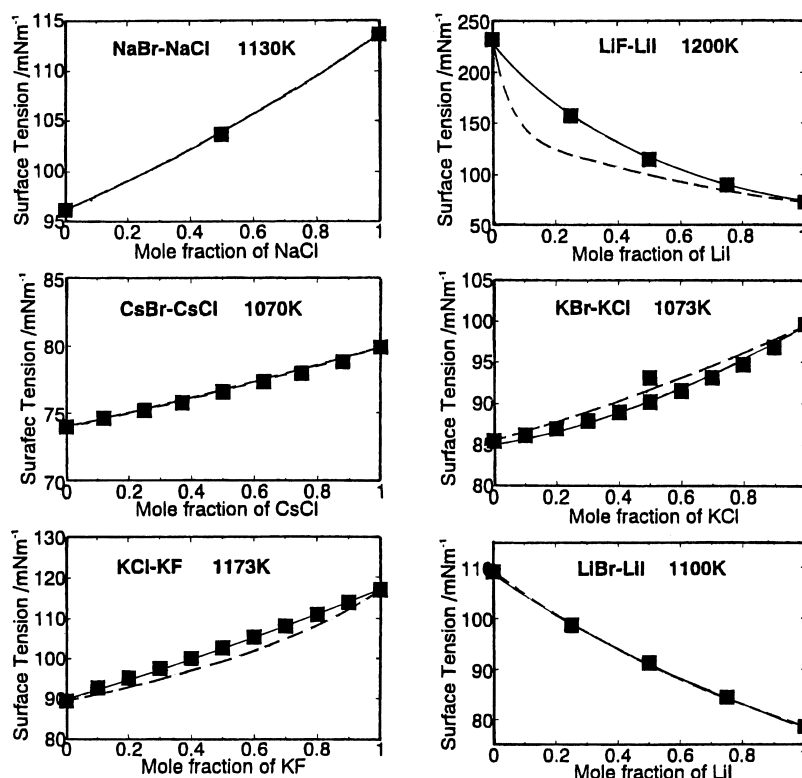
$$\beta^{MIX} = \frac{(Z^{Surf})'}{Z^{Bulk}} \cdot \frac{1}{\zeta^4} = 1.1 \quad : \quad \text{for molten ionic mixtures}$$

....(5)

In Eq. (5), we considered the effect of the surface relaxation on the change in ionic distance to keep charge neutrality on the surface.[10–13] $(Z^{Surf})'/Z^{Bulk}$ is the apparent ratio of the co-ordination number in the surface to that in the bulk $((Z^{Surf})'/Z^{Bulk}=0.94)$.[10–13] ζ is the ratio of change in the ionic distance at the surface to that in the bulk ($\zeta = 0.97$).[10–13] The calculated results of the surface tension of molten alkaline-halide systems obtained from Eq. (5) with

Fig. 3(c). Surface tension of molten ionic mixtures in common anion alkaline–halide systems. Dotted curves: from Eqs. (1), (2) and (4); solid curves: from Eqs. (6) and (7). ■: Expe. (Ref. 21).
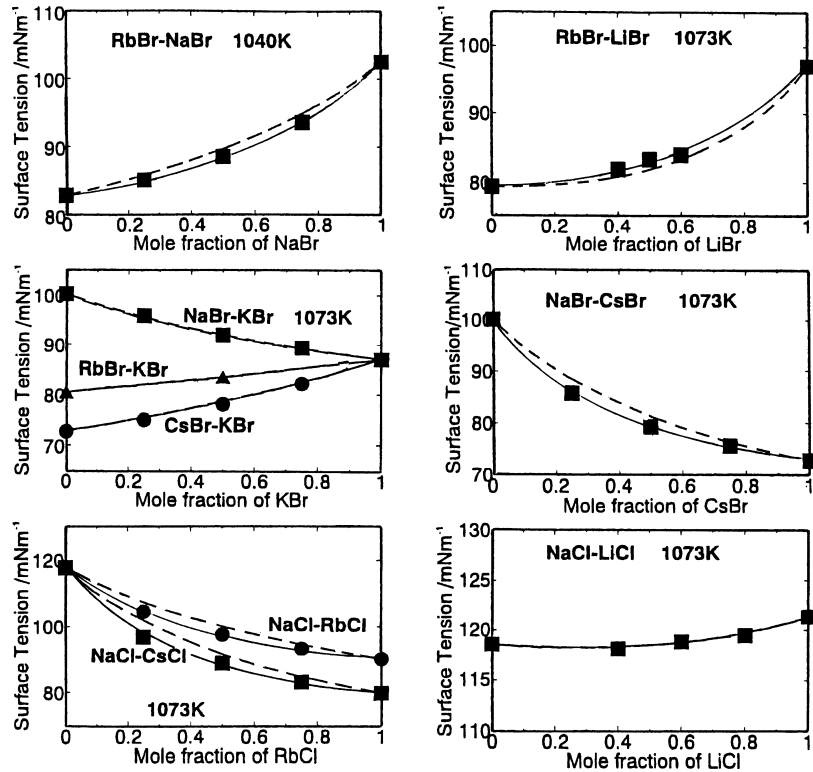

Fig. 3(d). Surface tension of molten ionic mixtures in common anion alkaline–halide systems. Dotted curves: from Eqs. (1), (2) and (4); solid curves: from Eqs. (6) and (7). ■: Expe. (Ref. 21).
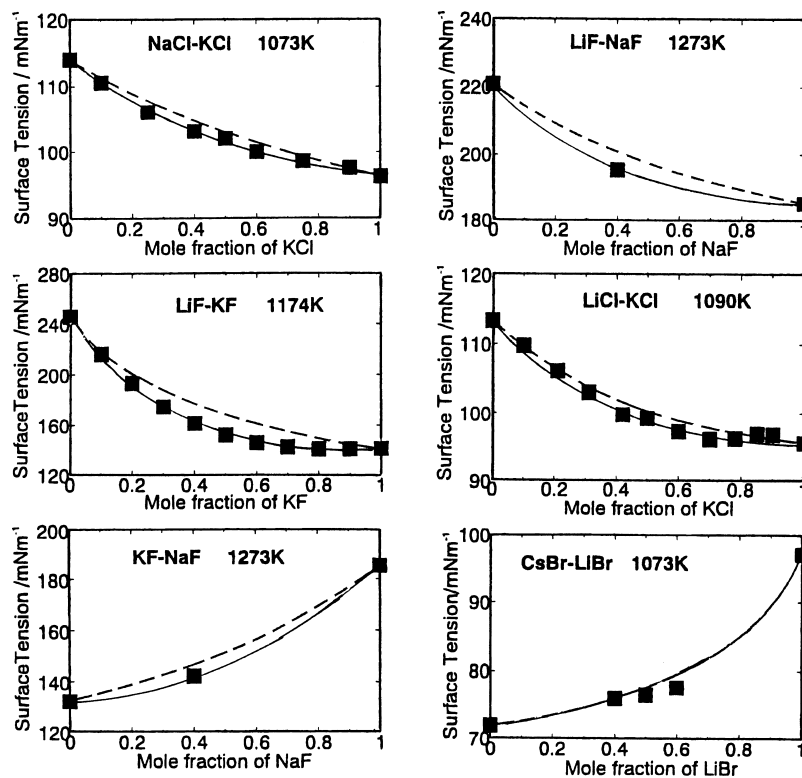
Eqs. (1), (2) and (3) are shown as dotted curves in **Figs. 3**(a)–3(d). As can be seen in these figures, the calculated results agree with the experimental ones[21] in many molten salt systems.[10,11] The authors have applied this approach to evaluate the surface tension of reciprocal systems, carbonates, sulfates, nitrates, molten slag[11-13] as well as the interfacial tension between liquid iron and molten slag.[13] However, we have noticed that we still have the following defects in this calculation:

1) In alkaline-halide molten ionic mixtures, there still exist some discrepancies between the calculated results and the experimental one. In particular, in common cation systems (Figs. 3(a) and 3(b)), their composition dependence of the experimental surface tension shows almost linear change. On the other hand, common anion systems (Fig. 3(c) and 3(d)) have concave feature in the composition dependence. However, the calculated results do not always reproduce those composition dependence.[10]

2) In CaO–SiO$_2$ binary system, activities of the components change drastically with the composition, but the surface tension of this system has gentle change with the composition, which means that the surface tension is not affected by the drastic change in the activities.[4,13]

4. Evaluation of Surface Tension of Molten Ionic Mixtures

The authors have derived the Eqs. (6) and (7) described below on the basis of the following assumptions for the above problems:

(1) It has been known that molten ionic mixtures easily have surface relaxation such as spontaneous change in ionic distance at the surface, which lets the energetic state of the surface approach the bulk state.[22]

(2) In ionic substances, it is well known that their ionic structures depend upon the ratio of the radius of cation to that of anion[23] as shown in **Fig. 4**. In order to evaluate ionic structure and physico-chemical properties of ionic materials, we should consider the ratio of the radius of cation to that of anion.

Then, we set the following conditions:

"1": In the above Eqs. (1) and (2), the surface structural relaxation is considered in the first term on the right-hand side, i.e. σ_i^{Prure}. In addition, the excess Gibbs energies in the surface are also affected by the surface relaxation, and they approach the excess Gibbs energies in the bulk. Then, it is assumed in the present work that we neglect the difference between the excess Gibbs energies in the surface and that in the bulk.

"2": We replace the mole fraction in Eqs. (1) and (2) by the ionic radius fraction considering the ratio of the radius of cation to that of anion.

Finally we have derived the following semi-empirical equations to evaluate the surface tension σ of molten ionic mixtures:

$$\sigma = \sigma_{AX}^{Pure} + \frac{RT}{A_{AX}} \ln \frac{M_{AX}^{Surf}}{M_{AX}^{Bulk}} \quad \dots\dots\dots\dots(6)$$

$$R = \frac{R_{Cation}}{R_{Anion}}$$

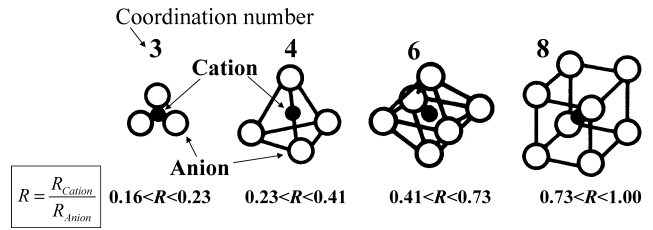| Coordination number	3	4	6	8
	0.16<R<0.23	0.23<R<0.41	0.41<R<0.73	0.73<R<1.00

Fig. 4. Correlation between ionic structure and the ratio of ionic radius of cation to that of anion through coordination number.

Table 1. Ionic radii in Å of cations and anions.

Li$^+$	0.60*	F$^-$	1.36*
Na$^+$	0.95*	Cl$^-$	1.81*
K$^+$	1.33*	Br$^-$	1.95*
Rb$^+$	1.48*	I$^-$	2.16*
Cs$^+$	1.69*	O^{2-}	1.44*
Ca^{2+}	0.99*	SO$_4^{2-}$	2.18**
Mg^{2+}	0.66*		
Fe^{2+}	0.74*		
Mn^{2+}	0.80*		

Ref. : * Shannon [24], ** Jenkins et al. [25,26]

$$\sigma = \sigma_{BY}^{Pure} + \frac{RT}{A_{BY}} \ln \frac{M_{BY}^{Surf}}{M_{BY}^{Bulk}} \quad \dots\dots\dots\dots(7)$$

Here,

$$M_{AX}^{P} = \frac{(R_A / R_X) \cdot N_{AX}^{P}}{(R_A / R_X) \cdot N_{AX}^{P} + (R_B / R_Y) \cdot N_{BY}^{P}},$$

$$M_{BY}^{P} = \frac{(R_B / R_Y) \cdot N_{BY}^{P}}{(R_A / R_X) \cdot N_{AX}^{P} + (R_B / R_Y) \cdot N_{BY}^{P}}$$

In the above equations, subscripts A and B are cations, and X and Y are anions. Superscripts $P=$Surf or Bulk indicate the surface and the bulk, respectively. R_A and R_B are the radius of cations, and R_X and R_Y are the radius of anions. The information on the radius of ions can be obtained from the compilation by Shannon[24] and they are summarized in **Table 1**. $A_i = N_0^{1/3} V_i^{2/3}$ (N_0: Avogadro's number, V_i: molar volume of pure component i) is the molar surface area of pure component i. The values of surface tension and density of pure molten salts[21] are listed in **Tables 2** and **3**. Molar volume of molten pure salt is calculated by dividing molecular weight (sum of atomic weight shown in Table 2) by the density.

The calculated results of the surface tension in various alkaline–halide ionic mixtures obtained from Eqs. (6) and (7) are shown by solid curves in Fig. 3. In all of the systems in Fig. 3, the calculated results (solid curves) agree well with the experimental values (■).[21] In addition, the model reproduces the characteristics of the composition dependence quite well in common ionic mixtures described above. Furthermore, this model can be applied to molten salt mixtures with complex anions such as sulfate systems. In those ionic mixtures, we used the apparent effective radii of complex anions proposed by Jenkins et al.,[25,26] who derived the radii to investigate other bulk properties. Some of the calculated results on sulfate systems are shown in **Fig.**

Table 2. Surface tension and density values of pure molten salts for common anion systems.

Molten salt mixtures	Temp. /K	Surface tension of pure molten salt / mNm⁻¹		Density of pure molten salts /10⁻³ kg·m⁻³
CsCl-CsI	1100	CsCl :	77.6	2.60
		CsI :	63.5	2.95
CsBr-CsI	1070	CsBr :	74.0	2.94
		CsI :	65.2	2.99
LiCl-LiF	1173	LiCl :	107.5	1.38
		LiF :	234.5	1.78
LiBr-LiCl	973	LiBr :	118.0	2.43
		LiCl :	134.0	1.46
RbBr-RbCl	1110	RbBr :	77.8	2.55
		RbCl :	87.4	2.14
LiBr-LiF	1130	LiBr :	107.1	2.33
		LiF :	238.8	1.80
NaBr-NaCl	1130	NaBr :	96.2	2.25
		NaCl :	113.7	1.53
LiF-LiI	1200	LiF :	231.9	1.77
		LiI :	72.9	2.69
CsBr-CsCl	1070	CsBr :	74.0	2.94
		CsCl :	79.9	2.63
KBr-KCl	1073	KBr :	85.5	2.07
		KCl :	99.4	1.51
KCl-KF	1173	KCl :	89.4	1.45
		KF :	117.0	1.88
LiBr-LiI	1100	LiBr :	109.2	2.35
		LiI :	78.6	2.78

Atomic weights : Element / AT / 10⁻³ kg·mol⁻¹

Li / 6.94, Na / 22.99, K / 39.09, Rb /85.47, Cs / 132.91,

F / 18.998, Cl / 35.453, Br / 79.904, I / 126.904,

S / 32.07, O / 16.00

Table 3. Surface tension and density values of pure molten salts from common anion systems.

Molten salt mixtures	Temp. /K	Surface tension of pure molten salt / mNm⁻¹		Density of pure molten salts /10⁻³ kg·m⁻³
RbBr-NaBr	1040	RbBr :	82.8	2.62
		NaBr :	102.5	2.33
RbBr-LiBr	1073	RbBr :	79.4	2.59
		LiBr :	97.0	2.37
NaBr-KBr	1073	NaBr :	100.2	2.30
		KBr :	87.1	2.07
RbBr-KBr	1073	RbBr :	80.4	2.59
		KBr :	87.1	2.07
CsBr-KBr	1073	CsBr :	72.7	2.93
		KBr :	87.1	2.07
NaBr-CsBr	1073	NaBr :	100.2	2.30
		CsBr :	72.7	2.93
NaCl-RbCl	1073	NaCl :	117.9	1.56
		RbCl :	90.1	2.17
NaCl-CsCl	1073	NaCl :	117.9	1.56
		CsCl :	79.8	2.63
NaCl-LiCl	1073	NaCl :	118.5	1.56
		LiCl :	121.4	1.42
NaCl-KCl	1073	NaCl :	114.0	1.56
		KCl :	96.3	1.51
LiF-NaF	1273	LiF :	220.7	1.73
		NaF :	185.2	1.95
LiF-KF	1174	LiF :	245.7	1.78
		KF :	141.7	1.88
LiCl-KCl	1090	LiCl :	113.3	1.41
		KCl :	95.7	1.50
KF-NaF	1273	KF :	132.1	1.82
		NaF :	185.2	1.95
CsBr-LiBr	1073	CsBr :	71.9	2.93
		LiBr :	97.0	2.37

5. The values of apparent effective radius of SO_4^{2-}, the surface tension and the density of pure molten salts are listed in Tables 1[25,26)] and 4.[21)]

5. Evaluation of Surface Tension of Molten SiO₂ based Binary Slag

In this section, we have extended the above model derived for molten ionic mixtures to molten SiO_2 based binary slags. Since the complex ion SiO_4^{4-} exits in molten SiO_2 systems, we assumed that Si^{4+} is cation, and SiO_4^{4-} is anion unit to evaluate the ratio $R=(R_{Anion}/R_{Cation})$ for SiO_2. However, we do not know the value of the ratio of the radius of Si^{4+} ion to that of SiO_4^{4-} ion, which is therefore treated as a parameter. The ionic radii of some ions such as Ca^{2+}, O^{2-} are listed in Table 1[24)] In addition, when we apply the above Eqs. (6) and (7) to molten slag, we need the information on the surface tension of pure molten oxides. We have had the value of the surface tension of molten pure $SiO_2(\sigma_{SiO_2}/mN\,m^{-1}=243.2+0.031\cdot T)$,[21)] but we usually do not have the information on the surface tension of, for example, pure liquid CaO at around 1 873 K because pure CaO exists as solid state at the temperature. Therefore, it is necessary to treat the surface tension of pure oxide components as another parameter at around 1 873 K.

We calculated the surface tension of molten binary SiO_2 based binary slags from Eqs. (6) and (7) with the following assumptions:

(1) We assume that the ratio of ionic radius of cation to that of anion for SiO_2 is regarded as the ratio of the radius
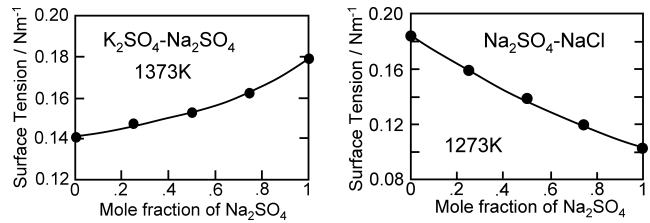

Fig. 5. Surface tension of molten ionic mixtures in sulfate systems. Solid curves: from Eqs. (6) and (7), ●: Expe. (Ref 21).

Table 4. Surface tension and density values of pure molten salts for sulfate systems.

Molten salt mixtures	Temp. /K	Surface tension of pure molten salt / mNm⁻¹		Density of pure molten salts /10⁻³ kg·m⁻³
K₂SO₄-Na₂SO₄	1373	K₂SO₄ :	140.6	1.86
		Na₂SO₄ :	178.4	1.97
Na₂SO₄-NaCl	1273	Na₂SO₄ :	185.0	2.01
		NaCl:	103.1	1.45

of Si^{4+} to that of SiO_4^{4-} $(R_{Si^{4+}}/R_{SiO_4^{4-}})$ which is determined to fit calculated results with experimental values.

(2) We determine the surface tension of pure components with high melting point, e.g. CaO by parameter-fitting to reproduce experimental values of the surface tension of molten slag.
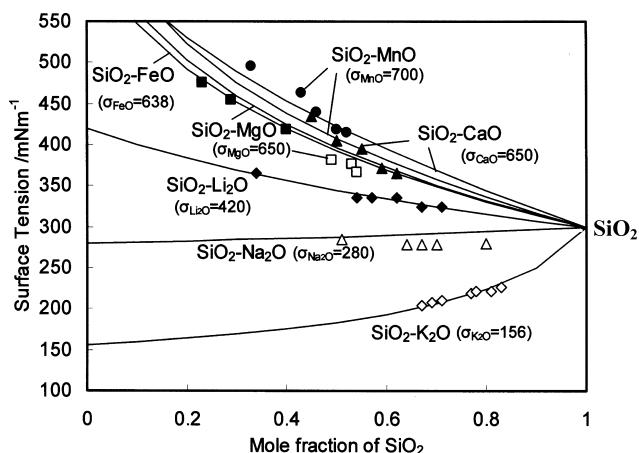
Fig. 6. Surface tension of molten SiO_2 based binary systems.

The calculated results are shown in **Fig. 6** with the experimental values reported by Boni & Derge.[27] In this calculation, we selected $R=(R_{Anion}/R_{Cation})=0.5$ as the ratio of the radius of Si^{4+} to that of SiO_4^{4-}. Furthermore, we selected the value of the surface tension of molten pure oxides in the parenthesis in Fig. 6. These parameters have been selected as best-fitting values to satisfy the calculated results with the experimental values. As shown in Fig. 6, we found that we could evaluate the surface tension of various molten SiO_2 based slag from Eqs. (6) and (7) although we need to select the values of $R=(R_{Anion}/R_{Cation})$ for SiO_2 and the surface tension of pure molten oxides. Based on the results obtained here, we suppose that the surface tension of molten slag can be predicted from the present model because the above Eqs. (6) and (7) can be easily extended to multi-component systems.

6. Concluding Remarks

We have derived the thermodynamic model to evaluate the surface tension of molten ionic mixtures by considering the ratio of the radius of cation to that of anion. The following results are obtained:

(1) Although the surface tension of molten alkaline–halide ionic mixtures has the following characteristics of the composition dependence;
- almost linear change with the composition in common cation systems,
- large concave feature of the composition dependence in common anion systems,

the present model reproduces the above composition dependences of molten ionic mixtures precisely.

(2) The surface tension of molten ionic mixtures with complex anion such as sulfate can be evaluated by considering effective ionic radii for the complex anions.

(3) When we assume the apparent ratio of the radius of Si^{4+} to that of SiO_4^{4-} as well as the surface tension of pure molten oxides, the surface tension of molten SiO_2 based binary slag can be evaluated from the present model.

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