<table>
<thead>
<tr>
<th>Title</th>
<th>Evaluation of Surface Tension of Molten Ionic Mixtures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Tanaka, Toshihiro; Kitamura, Tomoko; Back, Ida Annika</td>
</tr>
<tr>
<td>Citation</td>
<td>ISIJ International. 46(3) P.400-P.406</td>
</tr>
<tr>
<td>Issue Date</td>
<td>2006</td>
</tr>
<tr>
<td>Text Version</td>
<td>publisher</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/11094/26399">http://hdl.handle.net/11094/26399</a></td>
</tr>
<tr>
<td>DOI</td>
<td>10.2355/isijinternational.46.400</td>
</tr>
<tr>
<td>rights</td>
<td>© 2006 ISIJ</td>
</tr>
</tbody>
</table>

*Osaka University Knowledge Archive : OUKA*

https://ir.library.osaka-u.ac.jp/repo/ouka/all/

Osaka University
Evaluation of Surface Tension of Molten Ionic Mixtures

Toshihiro TANAKA,1) Tomoko KITAMURA1) and Ida Annika BACK2)

1) Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871 Japan. 2) Formerly at Division of Materials and Manufacturing Science, Osaka University, now at Åbo Akademi University, Turku, Finland.

(Received on July 29, 2005; accepted on January 11, 2006)

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 of molten alkaline–halide ionic mixtures with complex anion such as sulfate as well as molten SiO2 based binary systems considering effective ionic radii for complex anions.

KEY WORDS: surface tension; thermodynamics; molten slag; SiO2; ionic radius.

1. Introduction

Since surface tension of molten ionic mixtures such as molten slag is an important physico-chemical property 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 system1,5,6) by considering simultaneously both of phase equilibria and the surface properties. At the present stage, we can evaluate the surface tension of liquid alloys1–6) by using Butler’s equation7) 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 described later. Here, we use the following Eqs. (1) and (2) to evaluate the surface tension of liquid alloys. These equations were derived10 by one of the authors to re-investigate the derivation of Butler’s model.7) The formula is the same as that derived by Butler.7)

\[
\sigma = \sigma_{i}^{Pure} + \frac{RT}{A_i} \ln \left( \frac{N_i^{Surf}}{N_i^{Bulk}} \right) + \frac{1}{A_i} \left( G_i^{E,Surf}(T, N_i^{Surf}) - G_i^{E,Bulk}(T, N_i^{Bulk}) \right) \quad (1)
\]

\[
\sigma = \sigma_{B}^{Pure} + \frac{RT}{A_B} \ln \left( \frac{N_B^{Surf}}{N_B^{Bulk}} \right) + \frac{1}{A_B} \left( G_B^{E,Surf}(T, N_B^{Surf}) - G_B^{E,Bulk}(T, N_B^{Bulk}) \right) \quad (2)
\]

In Eqs. (1) and (2), \( \sigma_{i}^{Pure} \) is the surface tension of pure component \( i \), \( A_i = L N_i^{0.67} V_i^{2/3} \) (\( N_i \): 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. \( N_i^{0.67} \) is mole fraction of component \( i \) in the bulk (\( P = \text{Bulk} \)) and the surface (\( P = \text{Surf} \), \( G_i^{E,P}(T, N_i^{0.67}) \) is partial excess Gibbs energy of component \( i \) in the bulk (\( P = \text{Bulk} \)) and the surface (\( P = \text{Surf} \), which is a function of temperature \( T \) and the mole fraction of component B...
In Eqs. (1) and (2), \( G_{E,Bulk}(T, N_{B,\text{Bulk}}) \) in the bulk can be obtained directly from thermodynamic databases, but \( G_{E,\text{Surf}}(T, N_{B,\text{Surf}}) \) for the surface can be estimated from the following approximation proposed by Speiser et al. \( ^{8,9} \):

\[
\frac{G_{E,\text{Surf}}(T, N_{B,\text{Surf}})}{H_{11005}^{\beta_{\text{MIX}}}} = \frac{G_{E,Bulk}(T, N_{B,\text{Surf}})}{H_{11005}^{\beta_{\text{MIX}}}} 
\]

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 \( N_{B,\text{Surface}} \). \( b_{\text{MIX}} \) is a parameter related to the ratio of the coordination number in the surface to that in the bulk \( Z_{\text{Surf}}/Z_{\text{Bulk}} \). For example, Speiser et al. \( ^{8,9} \) proposed \( \beta_{\text{MIX}} = (Z_{\text{Surf}}/Z_{\text{Bulk}})^{9/12} = 0.75 \) by assuming a closed packed solid structure. However, since the value \( \beta_{\text{MIX}} \) for liquid cannot be evaluated exactly, the authors determined the apparent ratio of \( (Z_{\text{Surf}}/Z_{\text{Bulk}})^{0.94} \) for liquid metals and alloys from the relationship between the surface tension of pure metals and the binding energy per unit area \( ^{1-6,10-13} \):

\[
\beta_{\text{MIX}} = \frac{(Z_{\text{Surf}})^{0.83}}{Z_{\text{Bulk}}} : \text{ for pure metals and alloys} \ldots (4)
\]

The procedure to calculate the surface tension of liquid alloys \( \sigma \) 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 \( \sigma \) and the surface composition \( N_{B,\text{Surface}} \).
3. These equations are solved numerically to determine \( \sigma \) and \( N_{B,\text{Surface}} \).

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 \( N_{B,\text{Bulk}} \) and \( N_{B,\text{Surface}} \) 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 applied 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 \( \beta_{\text{MIX}} = (Z_{\text{Surf}}/Z_{\text{Bulk}})^{0.94} \), 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-
molten ionic mixtures by considering only the ratio of the coordination number in the surface to that in the bulk.\textsuperscript{10–13)} Then, we proposed the following equation to evaluate the value of $f_{\text{MIX}}^0$ to cope with the above problems in our previous work\textsuperscript{10–13)}:

\begin{equation}
\end{equation}

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

\textbf{Fig. 3(b).} Surface tension of molten ionic mixtures in common cation alkaline–halide systems. Dotted curve: from Eqs. (1), (2) and (4); solid curves: from Eqs. (6) and (7). \textbullet\ Expe. (Ref. 21).
\[ \beta^{\text{MIX}} = \left( \frac{Z_{\text{Surf}}}{Z_{\text{Bulk}}} \right) \frac{1}{\zeta^4} = 1.1 \] for molten ionic mixtures.

In Eq. (5), we considered the effect of the surface relaxation on the change in ionic distance to keep charge neutrality on the surface. \( \left( \frac{Z_{\text{Surf}}}{Z_{\text{Bulk}}} \right) \frac{1}{\zeta^4} \) is the apparent ratio of the coordination number in the surface to that in the bulk. \( \zeta \) is the ratio of change in the ionic distance at the surface to that in the bulk. \( \zeta = 0.97 \) in the calculations of the surface tension of molten alkaline-halide systems obtained from Eq. (5) with the experimental data (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 in many molten salt systems. The authors have applied this approach to evaluate the surface tension of reciprocal systems, carbonates, sulfates, nitrates, molten slag as well as the interfacial tension between liquid iron and molten slag. 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 that composition dependence.

2) In CaO–SiO2 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. 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.

(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 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. $\sigma_{\text{pure}}$. 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 $\sigma$ of molten ionic mixtures:

$$\sigma = \sigma_{\text{pure}} + \frac{RT}{A_{\text{AX}}} \ln \frac{M_{\text{AX}}^{\text{surf}}}{M_{\text{AX}}^{\text{bulk}}} \quad \text{.(6)}$$

Here,

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

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

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 and they are summarized in Table 1. $A_i = N_{i0}^{\text{AV}} V_i^{\text{AV}}$ ($N_{i0}$: 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 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 (■). 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., who derived the radii to investigate other bulk properties. Some of the calculated results on sulfate systems are shown in Fig.

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

<table>
<thead>
<tr>
<th>Ion</th>
<th>Radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li+</td>
<td>0.606</td>
</tr>
<tr>
<td>Na+</td>
<td>0.95</td>
</tr>
<tr>
<td>K+</td>
<td>1.33</td>
</tr>
<tr>
<td>Rb+</td>
<td>1.48</td>
</tr>
<tr>
<td>Cs+</td>
<td>1.69</td>
</tr>
<tr>
<td>Ca2+</td>
<td>0.99</td>
</tr>
<tr>
<td>Mg2+</td>
<td>0.66</td>
</tr>
<tr>
<td>Fe2+</td>
<td>0.74</td>
</tr>
<tr>
<td>Mn2+</td>
<td>0.80</td>
</tr>
</tbody>
</table>

Ref. : * Shannon, ** Jenkins et al.
5. The values of apparent effective radius of \( \text{SO}_4^{2-} / \text{H}_2\text{O} \), the surface tension and the density of pure molten salts are listed in Tables 1, 2, and 4. \( ^{24} \)

5. Evaluation of Surface Tension of Molten \( \text{SiO}_2 \) based Binary Slag

In this section, we have extended the above model derived for molten ionic mixtures to molten \( \text{SiO}_2 \) based binary slags. Since the complex ion \( \text{SiO}_4^{4-} / \text{H}_2\text{O} \) exists in molten \( \text{SiO}_2 \) systems, we assumed that \( \text{Si}^{4+} / \text{H}_2\text{O} \) is cation, and \( \text{SiO}_4^{4-} / \text{H}_2\text{O} \) is anion unit to evaluate the ratio \( R = (R_{\text{Anion}} / R_{\text{Cation}}) \) for \( \text{SiO}_2 \). However, we do not know the value of the ratio of the radius of \( \text{Si}^{4+} \) ion to that of \( \text{SiO}_4^{4-} \) ion, which is therefore treated as a parameter. The ionic radii of some ions such as \( \text{Ca}^{2+} / \text{H}_2\text{O} \), \( \text{O}^{2-} / \text{H}_2\text{O} \) 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 \( \text{SiO}_2 (\sigma_{\text{SiO}_2}/\text{mN m}^{-1} = 243.2 + 0.031 \times T) \), \( ^{21} \) but we usually do not have the information on the surface tension of, for example, pure liquid CaO at around 1873 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 1873 K.

We calculated the surface tension of molten binary \( \text{SiO}_2 \) 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 \( \text{SiO}_2 \) is regarded as the ratio of the radius of \( \text{Si}^{4+} \) to that of \( \text{SiO}_4^{4-} (R_{\text{Si}^{4+}} / R_{\text{SiO}_4^{4-}}) \) 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.

\( ^{21} \)
The calculated results are shown in Fig. 6 with the experimental values reported by Boni & Derge. In this calculation, we selected \( R = \frac{R_{\text{Anion}}}{R_{\text{Cation}}} = 0.5 \) as the ratio of the radius of \( \text{Si}^{4+} \) to that of \( \text{SiO}_4^{2-} \). 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 \( \text{SiO}_2 \) based slag from Eqs. (6) and (7) although we need to select the value of \( R = \frac{R_{\text{Anion}}}{R_{\text{Cation}}} \) for \( \text{SiO}_2 \) 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 \( \text{Si}^{4+} \) to that of \( \text{SiO}_2^{2-} \) as well as the surface tension of pure molten oxides, the surface tension of molten \( \text{SiO}_2 \) based binary slag can be evaluated from the present model.

REFERENCES