THERMODYNAMIC EVALUATION OF SURFACE TENSION OF MOLTEN SALT MIXTURES

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The thermodynamic model has been derived for the surface tension of molten salt mixtures in common ion alkali-halide systems considering the relaxation structure of the surface and the ionic sizes, and it has been extended to molten salt mixtures in common ion alkali-nitrate, carbonate and sulfate systems, and binary oxide systems to discuss the composition dependence of the surface tension of those systems.

INTRODUCTION

The authors have applied thermodynamic databases, which are usually used for the calculation of phase diagrams, to the evaluation of surface tension of liquid alloys, molten salt mixtures and molten oxide mixtures(1-4). In those calculations, Butler's equation(5) for the surface tension of those mixtures has been applied with the approach proposed by Yeum et al.(6) to evaluate excess Gibbs energies in the surface. Although the above calculated results of the surface tension of liquid alloys agree well with experimental data, some calculated results for molten ionic mixtures show discrepancies with experimental data even for common ion alkali-halide systems(2-4).

In addition, we found that there exist a general relationship between the composition dependence of activity a_X in the bulk and that of the surface tension σ in liquid alloys (that is to say, positive deviation of a_X from ideal solution ⇔ negative deviation of σ, and vice versa), but this relationship is not applied to molten salt mixtures(2-4). Furthermore, the molten salt mixtures have the tendency to show the large downward curvature of the composition dependence of the surface tension(2-4,7).

In the previous work(3,4), the thermodynamic model was derived for the surface tension of molten salt mixtures in common ion alkali-halide systems considering the relaxation structure of the surface and the ionic sizes. The purpose of this work is to extend the above thermodynamic model to molten salt mixtures in common ion alkali-halide, nitrate, carbonate and sulfate mixtures, and binary oxide mixtures, and to discuss the composition dependence of the surface tension of those mixtures.
THERMODYNAMIC MODEL

The surface tension $\sigma$ of A-B binary molten ionic mixtures is evaluated from the combination of Eqs.[1] and [6] (3,4) when the information is used on fundamental physical properties of pure components and the excess Gibbs energies stored in some thermodynamic databases.

$$
\sigma = \sigma_A + \frac{RT}{A_A} \ln \left( \frac{(1-N_B^S)}{(1-N_B^B)} \right) + \frac{1}{A_A} \bar{G}_A^{E_S}(T,N_B^S) - \frac{1}{A_A} \bar{G}_A^{E_B}(T,N_B^B)
$$

$$
+ \frac{RT}{A_A} \ln \left( \frac{(1-N_B^B)}{(1-N_B^S)} \right) \frac{d_A+N_B^B d_B}{d_A+N_B^S d_B}
$$

$$
= \sigma_B + \frac{RT}{A_B} \ln \left( \frac{N_B^S}{N_B^B} \right) + \frac{1}{A_B} \bar{G}_B^{E_S}(T,N_B^S) - \frac{1}{A_B} \bar{G}_B^{E_B}(T,N_B^B)
$$

$$
+ \frac{RT}{A_B} \ln \left( \frac{(1-N_B^B)}{(1-N_B^S)} \right) \frac{d_A+N_B^B d_B}{d_A+N_B^S d_B}
$$

The above equation has been derived by considering the ionic distance fraction in the terms of the mixing entropy of Butler's equation(5). In the above equation, superscripts S and B show a surface phase and a bulk phase, respectively. $R$ : the gas constant, $T$ : temperature, $\sigma_X$ : surface tension of pure liquid $X$, $A_X = N_0^{1/3} V_X^{2/3}$ : molar surface area in a monolayer of pure liquid $X$, $(N_0 : \text{Avogadro number, } V_X : \text{molar volume of pure liquid } X)$, $N_B^S$ or $B$ : mole fraction of component $B$. $d_X$ is the ionic distance between cation and anion for pure salt $X$ and is assumed to be the sum of the radius of cation and that of anion for pure salt $X$. $\bar{G}_X^{E_S}(T,N_B^S)$ and $\bar{G}_X^{E_B}(T,N_B^B)$ : partial excess Gibbs energies of $X$ in the surface phase and the bulk phase as a function of $T$ and $N_B^S$ or $B$. $(X=A$ or $B)$ The information on $\bar{G}_X^{E_B}(T,N_B^B)$ in the bulk can be obtained from thermodynamic databases which are usually applied to the calculation of phase diagrams.

$\bar{G}_X^{E_S}(T,N_B^S)$ in the surface has been evaluated as follows(3,4):

The partial excess Gibbs energy $\bar{G}_X^{E_B}(T,N_B^B)$ in the bulk phase is assumed to be mainly determined by the polarization effect which is generated by the different ions having the same charge sign(3,4). Then, in the bulk phase,

$$
\bar{G}_X^{E_B}(T,N_B^B) \propto \alpha Z^B \left( \frac{1}{d_A^2} - \frac{1}{d_B^2} \right)^2
$$
where $\alpha$ is the polarization factor. The above equation is based on the idea proposed by Lumsden(8) although the effect of the London force on the excess Gibbs energy is ignored here.

In the surface phase, the following equation for the partial excess Gibbs energy $\bar{G}^{\text{Ex}}_{X}(T,N_{B}^{S})$ is assumed corresponding to the above equation[2]:

$$
\bar{G}^{\text{Ex}}_{X}(T,N_{B}^{S}) \propto \alpha (Z^{S}) \{ \frac{1}{(\zeta d_{A})^{2}} - \frac{1}{(\zeta d_{B})^{2}} \}^{2} = \alpha (Z^{S}) \left( \frac{1}{d_{A}^{2}} - \frac{1}{d_{B}^{2}} \right)^{2} \frac{1}{\zeta^{4}}
$$

[3]

Here, $\zeta$ is the ratio of the ionic distance in the surface phase to that in the bulk phase, which is caused by the relaxation in the surface. This $\zeta$ has been evaluated as about 0.97 by Sawada and Nakamura(9). When the ratio of $\bar{G}^{\text{Ex}}_{X}(T,N_{B}^{S})$ in Eq.[3] to $\bar{G}^{\text{Ex}}_{X}(T,N_{B}^{B})$ in Eq.[2] is expressed by replacing $N_{B}^{B}$ in Eq.[2] by $N_{B}^{S}$, we have obtained the following equation for molten ionic mixtures:

$$
\frac{\bar{G}^{\text{Ex}}_{X}(T,N_{B}^{S})}{\bar{G}^{\text{Ex}}_{X}(T,N_{B}^{B})} = \frac{(Z^{S})}{Z^{B}} \frac{1}{\zeta^{4}} = \frac{\beta^{1}}{\zeta^{4}}
$$

[4]

where $\beta^{1} = (Z^{S})/Z^{B}$ is the apparent ratio of the coordination number in the surface to that in the bulk considering the relaxation of the surface.

$\beta^{1}$ has been determined as follows(3,4):

After the surface is created from the bulk, we assume that some of the binding energy in the surface $U_{X}^{S}$ is consumed to form the relaxation structure in the surface, and the difference between the rest of the energy in the surface and the binding energy in the bulk $U_{X}^{B}$ can be seen as the surface tension $\sigma_{X}$ multiplied by molar surface area $A_{X}$. Then,

$$
\sigma_{X} A_{X} = (U_{X}^{S} - \Delta E_{X}) - U_{X}^{B}
$$

$$
= (1 - \beta^{1}) \cdot \Delta H_{\text{Eva},X}
$$

[5]

where $U_{X}^{B}$ and $U_{X}^{S} = (Z^{S}/Z^{B}) U_{X}^{B}$ are binding energies of component X in the bulk phase and the surface phase respectively, $\Delta H_{\text{Eva},X} = (-U_{X}^{B})$ : the evaporation energy of component X at melting point. $\Delta E_{X} = -(\xi/Z^{B}) U_{X}^{B}$ : the energy to form the relaxation structure in the surface. $\beta^{1} = (Z^{S} + \xi)/Z^{B}$ is the apparent ratio of the coordination number in the surface to that in the bulk.
the linear relation between $\sigma_X$ and $\Delta H_{\text{Evax}}/A_X$, the average value of $\beta'$ has been determined to be 0.94 for molten ionic mixtures and oxide mixtures (2-4). Substituting $\beta'=0.94$ and $\zeta^s=0.97(12)$ into Eq.[4], we obtain finally

$$\frac{\overline{G}_X^{\text{Ex},S}(T,N_B^S)}{G_X^{\text{Ex},P}(T,N_B^S)} = \frac{\beta'}{\zeta^4} = 1.1$$

**PROCEDURE FOR CALCULATION OF SURFACE TENSION OF MOLTEN SALT MIXTURES**

The surface tension $\sigma$ in Eq.[1] of molten ionic mixtures can be calculated as follows:

1) Inserting the values for surface tension $\sigma_X$ and molar surface area $A_X$ of pure liquid substances at a given temperature in Eq.[1].
2) Determining the excess Gibbs energies in the bulk phase at a given temperature and composition from thermodynamic databases, and substituting them in Eq.[1].
3) One pair between the two equations on the right-hand side of Eq.[1] becomes the equation with unknown $N_B^S$. This equation is solved for $N_B^S$.
4) The value of $N_B^S$ is substituted again into e.g. the first equation of the right-hand side of Eq.[1] to determine the surface tension $\sigma$ of the molten ionic mixtures on the left-hand side of Eq.[1].

**CALCULATED RESULTS AND DISCUSSION**

Figure 1 shows the calculated results of the surface tension of common ion alkali-halides, nitrates, carbonates and sulfates mixtures. In these calculations, we have applied a series of thermodynamic data on the excess Gibbs energy compiled by Pelton(10,11), and the data on the ionic radii summarized by Janz(12) and Shannon(13). As shown in Fig.1, the calculated results agree well with the experimental data(14) in those mixtures. As described in the previous work(3,4) on the common ion alkali-halide systems, it is found that in common cation systems, the composition dependence of the surface tension is slightly deviated from the linearity. On the other hand, in common anion systems, they have the large downward curvature of the composition dependence of the surface tension. These tendencies can be also seen in the common ion alkali-halides, nitrates, carbonates and sulfates mixtures.

Figure 2 shows the calculated results of the surface tension of molten CaO-SiO$_2$ binary oxide system. Gaye's model (15) has been applied to express the excess Gibbs
energy of molten oxide mixtures in this calculation. The data has been used on the surface tension of pure CaO reported by Nakajima (16) and SiO2 in NIST molten salt databases (14) since these references give us the temperature dependence of the surface tension of these pure oxides. As can be seen in Fig.2, it is confirmed that the present model can be also applied to molten binary oxide systems although the calculated results depend upon the selection of the values on the surface tension of pure components.

CONCLUDING REMARKS

The thermodynamic models have been derived for the surface tension of molten ionic mixtures considering the surface relaxation and the ionic sizes. Based on the present approach, the surface tension can be evaluated by using the thermodynamic databases which have been constructed for the calculation of phase diagrams. In addition, we can develop a multi-functional thermodynamic databank system, which will be of wide applicability in the evaluation of physico-chemical properties of molten ionic mixtures with the simultaneous calculation of the phase diagrams.

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Figure 1  Calculated Results of Surface Tension of Common Ion Alkali-Halides, Nitrates, Carbonates and Sulfates Mixtures. ■:Expe.(14), ---:Calc.

Figure 2  Calculated Results of Surface Tension of Molten CaO-SiO₂ Binary Oxide System.