Evaluation of Surface Tension of Molten Salt Mixtures based on Thermodynamic Databases

Toshihiro Tanaka, Mahoba Ogawa, Tamotsu Ueda
and Shigeta Hara

Department of Materials Science and Processing,
Faculty of Engineering, Osaka University,
2-1 Yamadaoka, Suita, Osaka 565, Japan.
Tel. +81-6-879-7467

ABSTRACT

The authors discussed the application of thermodynamic solution databases, which have been constructed so far to calculate thermodynamic properties and phase diagrams, to the evaluation of surface tension of molten salt mixtures.

1. INTRODUCTION

During the last 30 years, various thermodynamic databases have been constructed to be mainly applied to the calculation of phase diagrams of alloys, salts and oxides[1]. The accumulation and assessment of thermodynamic data and phase equilibrium information to establish those databases is sometimes called CALPHAD (Computer **Cal**culation of **Phas**e **D**iagrams) approach(2), which has been recognized to be useful in various aspects of materials science and engineering[1,2].

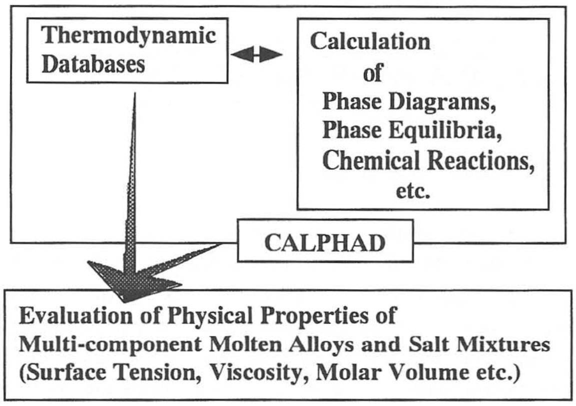

Figure 1 CALPHAD Approach and its Extension to Evaluate Physical Properties of Melts.

If it would be possible to use the thermodynamic databases to evaluate physical properties of liquid solutions as well as phase equilibria as shown in Fig.1, we could enlarge not only the utility of those thermodynamic databases but also the understanding of the physical properties of the liquid solutions. The authors have applied the thermodynamic databases to the evaluation of the surface tension of liquid alloys and molten ionic mixtures[3,4,5]. We still have some discrepancies of the calculated results with experimental values in some molten salt mixtures, which show large downward curvatures of the composition dependence of the surface tension of those mixtures. In the present work, we discuss some thermodynamic considerations to the evaluation of surface tension of molten salt mixtures in some common ion systems to fit the calculated results with the experimental values of the surface tension of those solutions.

2. THERMODYNAMIC EQUATIONS FOR SURFACE TENSION OF SOLUTIONS

We have applied the combination of the thermodynamic treatments by Butler [6], Speiser et al. [7,8] and Monma & Sudo [9] to evaluate surface tension σ of A-B binary liquid solutions [4,5]. Butler derived the following equation [1] assuming an equilibrium between a bulk phase and a surface phase[6]. The surface phase is regarded as a hypothetical independent phase and consists of the outermost monolayer of the surface as shown in Fig.2.

$$\begin{aligned}\sigma &= \sigma_A + \frac{RT}{A_A}\ln\frac{(1-N_B^S)}{(1-N_B^B)} + \frac{1}{A_A}\bar{G}_A^{E,S}(T,N_B^S) - \frac{1}{A_A}\bar{G}_A^{E,B}(T,N_B^B) \\ &= \sigma_B + \frac{RT}{A_B}\ln\frac{N_B^S}{N_B^B} + \frac{1}{A_B}\bar{G}_B^{E,S}(T,N_B^S) - \frac{1}{A_B}\bar{G}_B^{E,B}(T,N_B^B) \qquad [1]\end{aligned}$$

where R is the gas constant, T temperature, σ_X surface tension of pure liquid X, A_X molar surface area in a monolayer of pure liquid X (X=A or B).

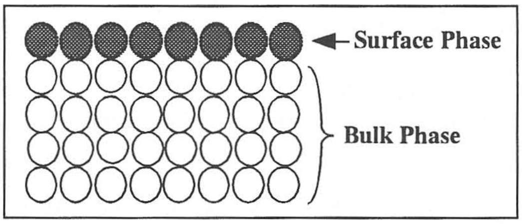

Figure 2 Equilibrium between "Surface Phase" and "Bulk Phase".

A_X in Eq.[1] can be obtained from the following equation.

$$A_X = LN_0^{1/3}V_X^{2/3} \qquad [2]$$

N_0 Avogadro number, V_X molar volume of pure liquid X. L in Eq.[2] is set to be unity for molten salts[4,5]. N_X^S and N_X^B in Eq.[1] are mole fractions of a component X in the surface phase and the bulk phase, respectively; $\bar{G}_X^{E,S}(T,N_B^S)$ in Eq.[1] is the partial excess Gibbs energy of X in the surface phase as a function of T and N_B^S ; $\bar{G}_X^{E,B}(T,N_B^B)$ partial excess Gibbs energy of X in the bulk phase as a function of T and N_B^B (X=A or B).

Since $\bar{G}_X^{E,B}(T,N_B^B)$ in the bulk phase in Eq.[1] can be obtained directly from thermodynamic databases, we only need the additional information on $\bar{G}_X^{E,S}(T,N_B^S)$ in the surface phase. Speiser et al.[7,8] proposed their own models for $\bar{G}_X^{E,S}(T,N_B^S)$ as follows[3,4,5]:

$$\bar{G}_X^{E,S}(T,N_B^S) = \beta \cdot \bar{G}_X^{E,B}(T,N_B^S) \qquad [3]$$

Speiser et al.[7,8] proposed β=3/4 for molten alloys, but we have determined the values of β for molten alloys and molten salt mixtures on the basis of the trial by Monma & Sudo[9] as follows [4,5]:

The surface tension σ_X of pure molten salt X at its melting point is assumed to be determined by the following relation.

$$\begin{aligned} A_X \cdot \sigma_X &= LN_0^{1/3}V_X^{2/3} \cdot \sigma_X \\ &= (-U_X^B) - (-U_X^S) \\ &= (-U_X^B) - \beta^* \cdot (-U_X^B) \\ &= (1-\beta^*) \cdot \Delta H_{Eva,X} \end{aligned} \qquad [4]$$

where U_X^B and U_X^S are binding energies of X in the bulk phase and the surface phase, and $\beta^* = U_X^S/U_X^B$. In the above equation, the surface entropy terms are neglected, and $(-U_X^B)$ is assumed to be approximately equal to evaporation energy $\Delta H_{Eva,X}$ of X at the melting point. Furthermore, we assume the following relation;

$$\begin{aligned} \beta^* (&= U_X^S/U_X^B) \quad \text{: for pure substances} \\ &= \beta\{=\bar{G}_X^{E,S}(T,N_B^S)/\bar{G}_X^{E,B}(T,N_B^S)\} \text{ : for solutions} \end{aligned} \qquad [5]$$

From the linear relation between σ_X and $\Delta H_{Eva}/(LN_0^{1/3}V_X^{2/3})$ in Eq.[4] and the above assumption in Eq.[5], we have determined β as follows [4,5] :

β=0.83 for liquid alloys [6]

β=0.94 for molten salt mixtures and oxide mixtures [7]

3. PROCEDURE OF CALCULATION OF SURFACE TENSION OF SOLUTIONS

The surface tension σ of a solution can be calculated as follows:

<1> Setting T and N_B^B of a solution. <2> Determining the values for σ_X, V_X and excess Gibbs energies in the bulk phase at the above T and N_B^B, 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, and the value of N_B^S is substituted again into e.g. the first equation of the right-hand side of Eq.[1] to calculate the surface tension σ on the left-hand side of Eq.[1].

4. APPLICATION OF THERMODYNAMIC DATABASES TO EVALUATION OF SURFACE TENSION OF MOLTEN SALT MIXTURES

We have used Pelton's thermodynamic database[10,11], which has been assessed to provide calculation of thermodynamic properties and phase diagrams of salt mixtures according to the CALPHAD approach, to calculate the surface tension of some molten salt mixtures. Common ion systems consisting of the following ions have been treated here:

Cations : Li^+, Na^+, K^+, Rb^+, Cs^+
Anions : F^-, Cl^-, Br^-, I^-

Surface tension data of pure component salts, σ_X in Eq.[1], were taken from the NIST database[12]. We obtained V_X in Eq.[2] from the selected density of pure component salts in the NIST database[12] with the molar weights of cations and anions. Figures 3 and 4 shows the comparison of the calculated results obtained from Eqs.[1], [2], [3] and [7] for the surface tension of various molten salt mixtures with the experimental values stored in NIST database[12]. As can be seen from these figures, the calculated results in common cation systems in Fig.3 agree with the experimental data, but in common anion systems in Fig.4, there exist some discrepancies in some molten salt mixtures, which have large downward curvatures of the composition dependence of the surface tension, although the discrepancies are almost within the uncertainties of the experimental values [4,5].

5. ADDITIONAL CONDITIONS FOR CALCULATION OF SURFACE TENSION OF MOLTEN SALT MIXTURES

5.1 Consideration of Relaxation Layer

In ionic solutions, the interaction between different ions extends over the outermost monolayer of the surface because of their Coulomb's force, which is one of the long-distance forces. In the previous work[5], as a possible way to derive an alternative equation for Eq.[3] considering those interactions among ions, we introduced the "relaxation layer" between the surface phase and the bulk phase. The relaxation layer is considered to be within the bulk phase region, but to be influenced by the surface phase. An equation has been proposed as shown in Eq.[8][5].

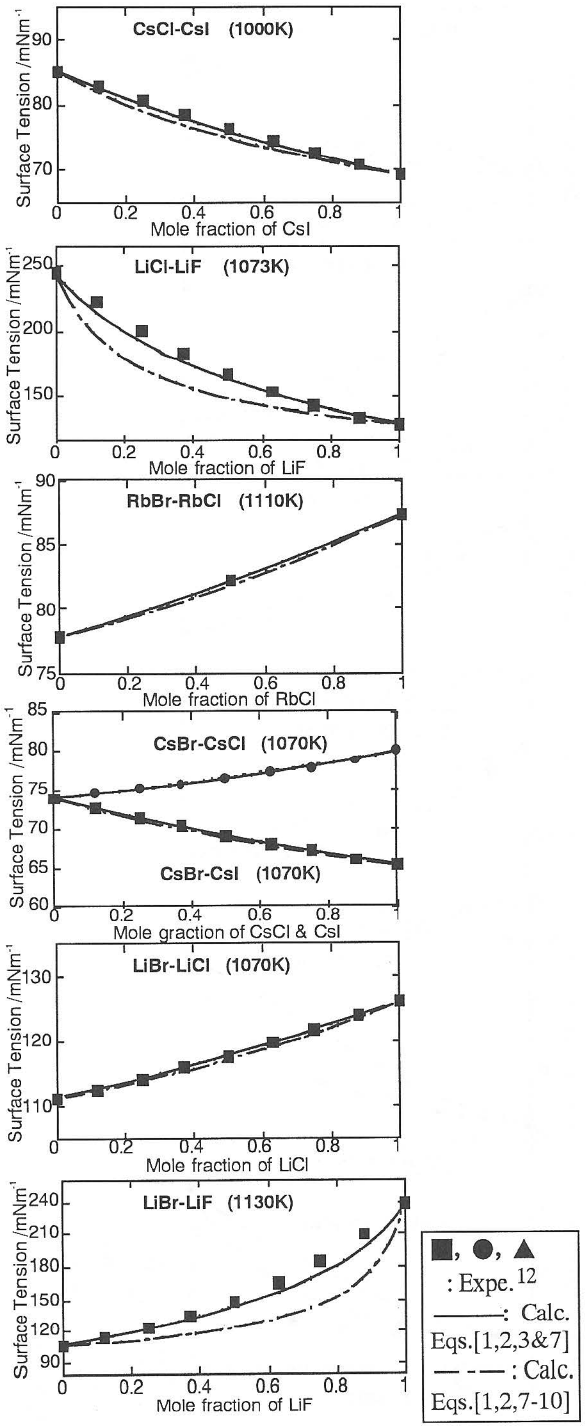

Figure 3 Calculated Results for the Surface Tension of Molten Sal Mixtures in Common Cation Systems with the Experimental Values [12].

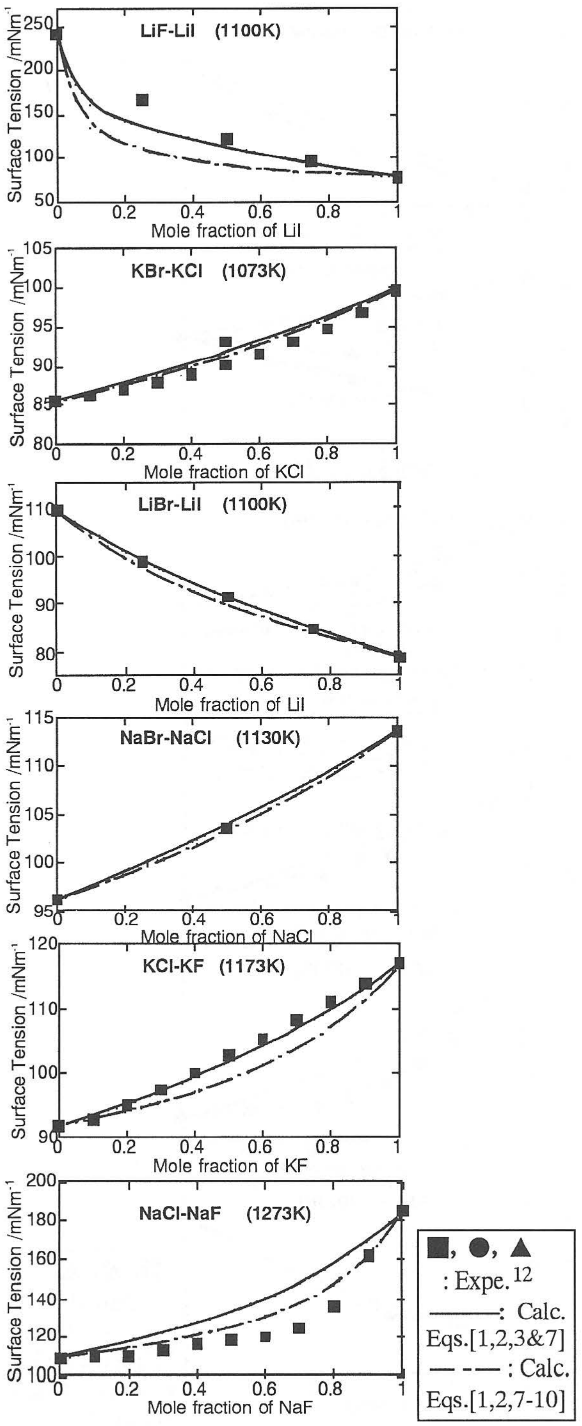

Figure 3 (Continued) Calculated Results for the Surface Tension of Molten Sal Mixtures in Common Cation Systems with the Experimental Values [12].

$$\bar{G}_X{}^{E,S}(T,N_B{}^S) = \beta \cdot \bar{G}_X{}^{E,B}(T,N_B{}^S) + S \cdot \bar{G}_X{}^{E,B}(T,N_B{}^B) \qquad [8]$$

In Eq.[8], the first term in the right-hand side shows the contribution of the interaction among ions in the outermost monolayer, and the second term shows the contribution of the relaxation layer, i.e., the effect of the interaction among ions in the surface phase to the bulk phase region, which is

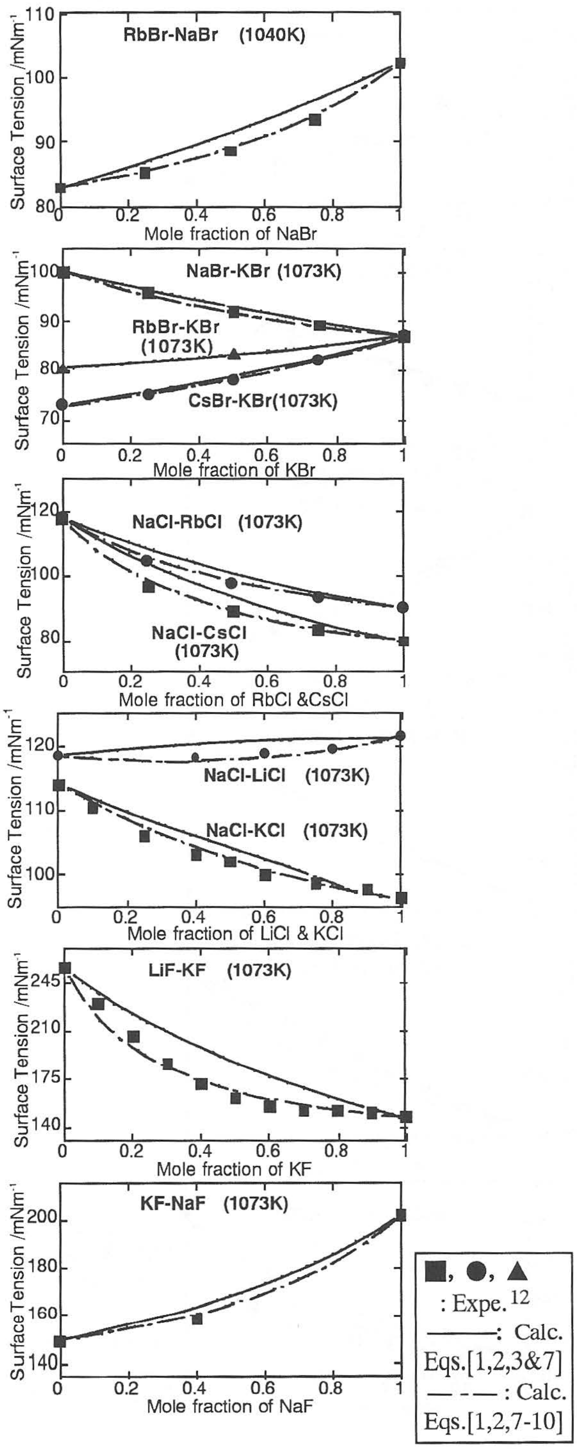

Figure 4 Calculated Results for the Surface Tension of Molten Sal Mixtures in Common Anion Systems with the Experimental Values[12].

a function of temperature T and the mole fraction of B in the bulk phase, N_B^B. The value of S shows the fraction of the effect of the relaxation layer to $\bar{G}_X^{E,S}(T,N_B^S)$.

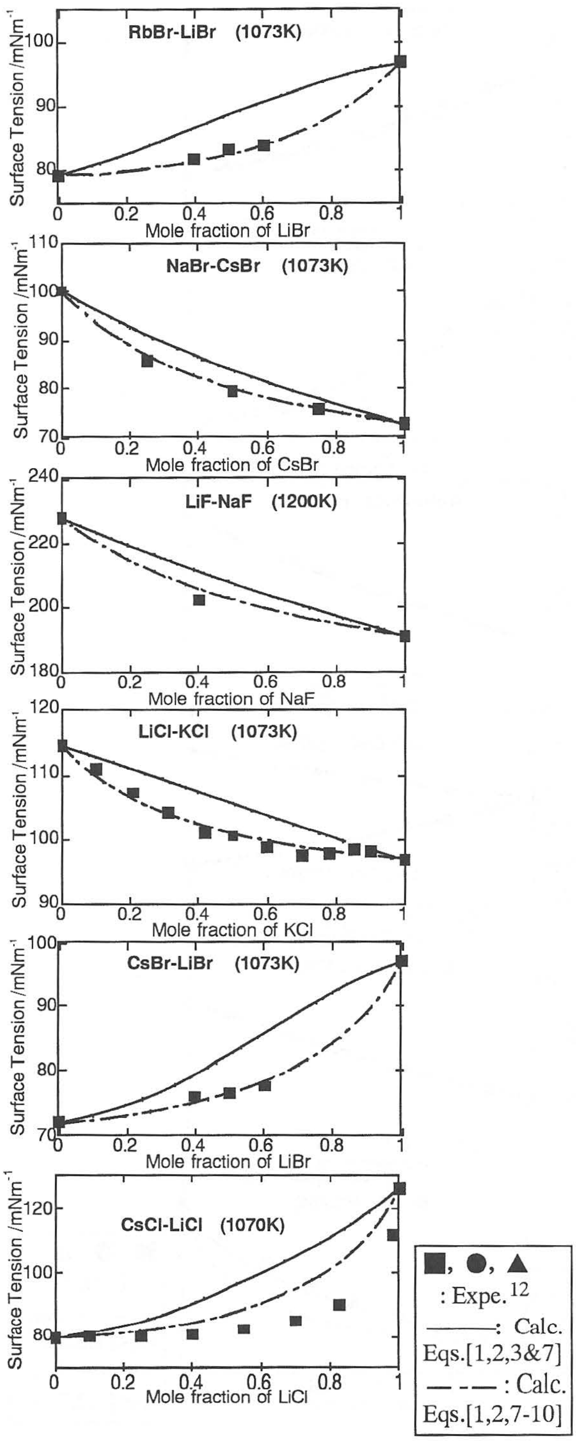

Figure 4 (Continued) Calculated Results for the Surface Tension of Molten Sal Mixtures in Common Anion Systems with the Experimental Values[12].

5.2 Consideration of Volume Fractions

In the present work, we have also introduced the idea proposed by Grjotheim et al.[13] and the recent trial by

Ye & Sahai[14] to consider the following volume fractions $N_{V,B}^{B}$ and $N_{V,B}^{S}$ instead of N_B^B and N_B^S in Eqs.[1] and [8] as follows :

$$N_{V,B}^{B} = V_B N_B^{B} / \{V_A(1-N_B^{B}) + V_B N_B^{B}\} \qquad [9]$$
$$N_{V,B}^{S} = V_B N_B^{S} / \{V_A(1-N_B^{S}) + V_B N_B^{S}\} \qquad [10]$$

The above two groups described that they obtained the downward curvatures of the composition dependencies of the surface tension of molten salt mixtures when they adopted the volume fractions in Guggenheim's equation[15] for the surface tension of ideal binary solutions.

The chain curves in Figs. 3 and 4 show the calculated results from the combination of Eqs.[1], [2], [7]~[10] when we set the value of S in Eq.[8] to be 0.1. As shown in these figures, the calculated results have been revised to agree with the experimental values in the common anion systems in Fig.4. On the other hand, the calculated results obtained from Eqs.[1], [2], [7]~[10] generate some discrepancies with the experimental values in the common cation systems as shown in Fig.3 for, e.g. LiCl-LiF, KCl-KF etc. When we compare the composition dependencies of molten salt mixtures in the common cation systems in Fig.3 with those in the common anion systems in Fig.4, we have found that the latter systems intend to have larger downward curvatures than the former systems.

We have carried out only the phenomenological discussion on the composition dependencies of molten salt mixtures in the present work. Furthermore, the value of S=0.1 was determined by a parameter-fitting procedure, and its physical meaning is still obscure. Therefore, in order to understand the surface tension of molten salt mixtures in more details from the standpoint of thermodynamic and microscopic view, we need the information of atomic structures near the surface and the further accumulation of the experimental data on the surface tension as well as thermodynamic properties of molten salt mixtures.

6. CONCLUDING REMARKS

The surface tensions of some molten salt mixtures in the common ion alkali-halide systems have been calculated using the thermodynamic data, which have been taken from the database assessed according to the CALPHAD approach. We have adopted some thermodynamic considerations to fit the calculated results with the experimental values. Although we still have some problems to revise the procedures to calculate the surface tension of molten salt mixtures, the present approach will enable us to develop a multi-functional thermodynamic databank system, which will be of wide applicability in the evaluation of physico-chemical properties of molten salt mixtures with the simultaneous calculation of the phase equilibria in those mixtures.

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