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Thermodynamic Evaluation of Surface Tension of Molten Salt Mixtures in Alkali Halides, Nitrate, Carbonate and Sulfate Systems

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

1 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 [94Tan, 96Tan, 98Tan1, 98Tan2, 98Tan3]. In those calculations, Butler's equation [32But] for the surface tension of those mixtures has been applied with the approach proposed by Speiser et al. [87Spe, 89Yeu] 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 [96Tan, 98Tan1, 98Tan2, 98Tan3]. In addition, we found that there exists a general relationship between the composition dependence of the 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 \leftrightarrow negative deviation of σ , and vice versa), but this relationship is not applied to molten salt mixtures [96Tan, 98Tan1, 98Tan2, 98Tan3]. Furthermore, the molten salt mixtures have the tendency to show a large downward curvature of the composition dependence of the surface tension [80Goo, 96Tan, 98Tan1, 98Tan2, 98Tan3, 98Tan4]. In the previous work [98Tan1, 98Tan2, 98Tan3], 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 for alkali halide mixtures to molten salt mixtures in common ion alkali halide, nitrate, carbonate and sulfate mixtures, and to discuss the composition dependence of the surface tension of those mixtures.

2 Thermodynamic Model

The surface tension σ of A–B binary molten ionic mixtures is evaluated from the combination of Eqs (1) and (8) [98Tan1, 98Tan2, 98Tan3] when the information is used on fundamental physical properties of pure components and the excess Gibbs energies stored in some thermodynamic databases.

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

The above equation has been derived by considering the ionic distance fraction in terms of the mixing entropy of Butler's equation. In the above equation, superscripts S and B indicate the surface and the bulk, respectively. R is the gas constant, T is the temperature, σ_X the surface tension of pure liquid X, $A_X = N_0^{1/3} V_X^{2/3}$ corresponds to the molar surface area in a monolayer of pure liquid X. (N_0 : Avogadro number, V_X : molar volume of pure liquid X). N_B^S or N_B^B is the 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 radii of the cation and that of the anion for pure salt X. $\bar{G}_X^{E,S}(T, N_B^S)$ and $\bar{G}_X^{E,B}(T, N_B^B)$ is the partial excess Gibbs energies of X in the surface and the bulk as a function of T and N_B^S or N_B^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 can be derived as follows [98Tan1, 98Tan2, 98Tan3].

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

$$\bar{G}_X^{Ex,B}(T, N_B^B) \propto \alpha Z^B \left(\frac{1}{d_A^2} - \frac{1}{d_B^2} \right)^2 \quad (2)$$

where α is the polarization factor. The above equation is based on an idea proposed by Lumsden [61Lum] although the effect of the London force on the excess Gibbs energy is ignored here. Z^B is the coordination number in the bulk.

In the surface, the following equation for the partial excess Gibbs energy $\bar{G}_X^{\text{Ex,S}}(T, N_B^S)$ is assumed corresponding to the above Eq. (2)

$$\begin{aligned} \bar{G}_X^{\text{Ex,S}}(T, N_B^S) &\propto \alpha (Z^S)' \left\{ \frac{1}{(\zeta d_A)^2} - \frac{1}{(\zeta d_B)^2} \right\}^2 = \\ &= \alpha (Z^S)' \left(\frac{1}{d_A^2} - \frac{1}{d_B^2} \right)^2 \frac{1}{\zeta^4} \end{aligned} \quad (3)$$

where $(Z^S)'$ is the apparent coordination number in the surface considering the relaxation of the surface as described later. ζ is the ratio of the ionic distance in the surface to that in the bulk, which is caused by the relaxation in the surface. This ζ has been evaluated as about 0.97 by Sawada and Nakamura [97Saw]. When the ratio of $\bar{G}_X^{\text{Ex,S}}(T, N_B^S)$ in Eq. (3) to $\bar{G}_X^{\text{Ex,B}}(T, N_B^B)$ 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

$$\beta^{\text{MIX}} = \frac{\bar{G}_X^{\text{Ex,S}}(T, N_B^S)}{\bar{G}_X^{\text{Ex,B}}(T, N_B^B)} = \left\{ \frac{(Z^S)'}{Z^B} \right\} \frac{1}{\zeta^4} = \frac{\beta'}{\zeta^4} \quad (4)$$

In Eq. (4), $\beta' = (Z^S)'/Z^B$. β' has been determined as follows [98Tan1, 98Tan2, 98Tan3].

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 σ_X multiplied by the molar surface area A_X . Then,

$$\sigma_X A_X = (U_X^S - \Delta E_X) - U_X^B \quad (5)$$

where U_X^B and $U_X^S = (Z^S/Z^B) U_X^B$ are binding energies of component X in the bulk and the surface, respectively. ΔE_X is the energy to form the relaxation structure in the surface. Although this was given by $-(\zeta/Z^B)U_X^B$ in the previous work [98Tan1, 98Tan2, 98Tan3], it has been modified in the present work to show that ΔE_X is assumed to be proportional to $(U_X^S - U_X^B)$ as follows

$$\Delta E_X = \lambda (U_X^S - U_X^B) = \lambda \left\{ \frac{Z^S}{Z^B} - 1 \right\} U_X^B \quad (6)$$

Then, Eq. (5) is

$$\begin{aligned} \sigma_X A_X &= \left[\frac{Z^S}{Z^B} U_X^B - \lambda \left\{ \frac{Z^S}{Z^B} - 1 \right\} U_X^B \right] - U_X^B = \\ &= \left\{ 1 - \frac{Z^S + \lambda (Z^B - Z^S)}{Z^B} \right\} \Delta H_{\text{Eva},X} = \\ &= \{1 - \beta'\} \Delta H_{\text{Eva},X} \end{aligned} \quad (7)$$

where $\Delta H_{\text{Eva},X} = (-U_X^B)$ is the evaporation energy of component X at the melting point. $\beta' = \{Z^S + \lambda (Z^B - Z^S)\}/Z^B = (Z^S)'/Z^B$ is the apparent ratio of the coordination number in the surface to that in the bulk considering the relaxation of the surface. The relation between σ_X and $\Delta H_{\text{Eva},X}/A_X$ for molten alkali halide salts is shown in Fig. 1 [96Tan, 98Tan1]. From the linear relation between σ_X and $\Delta H_{\text{Eva},X}/A_X$, the average value of β' has been determined to be 0.94 for molten alkali halide salts. If Z^S/Z^B is assumed to be $5/6 = 0.83$, $\lambda (Z^B - Z^S)/Z^B$

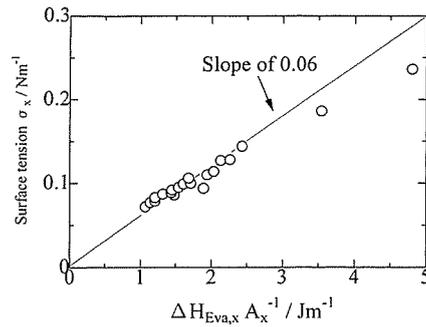


Fig. 1. Correlation of surface tension σ_x with $\Delta H_{\text{Eva},x} A_x^{-1}$ for pure alkali halide molten salts.

is about 0.11, in other words, ΔE_X is about 10% of $\sigma_X A_X = (U_X^S - \Delta E_X) - U_X^B$ in Eq. (5).

Substituting $\beta' = 0.94$ and $\zeta = 0.97$ into Eq. (4), we finally obtained [98Tan1, 98Tan2, 98Tan3]

$$\beta^{\text{MIX}} = \frac{\bar{G}_X^{\text{Ex,S}}(T, N_B^S)}{\bar{G}_X^{\text{Ex,B}}(T, N_B^B)} = \frac{\beta'}{\zeta^4} = 1.1 \quad (8)$$

The surface tension of molten salt mixtures in the common ion alkali halide systems can be evaluated by Eqs (1) and (8) as described in the previous work.

Although the information on $\Delta H_{\text{Eva},X}$ for alkali nitrate, carbonate and sulfate systems is not available, $\Delta H_{\text{Eva},X}$ can be associated to T_m as pointed out in [88lid] for liquid metals. Figure 2 shows the relationship between σ_X and T_m/A_X for various molten pure salts. Data for the plots of σ_X with T_m/A_X in Fig. 2 are listed in Table 1 [79Kub, 83Pel, 87NIS]. Comparing the gradient of the relation between σ_X and $\Delta H_{\text{Eva},X}/A_X$ in Fig. 1 with that of the relationship between σ_X and T_m/A_X in Fig. 2, we can estimate the value of β' for alkali nitrate, carbonate and sulfate systems as shown in Table 2. When the value of ζ is kept to be 0.97, the value of $\beta^{\text{MIX}} = \bar{G}_X^{\text{Ex,S}}(T, N_B^S)/\bar{G}_X^{\text{Ex,B}}(T, N_B^B)$ is determined to be 1.01 for those molten salts, which is different from $\beta^{\text{MIX}} = 1.1$ for alkali halide systems. Therefore, we have to investigate the value of β^{MIX} for molten salt mixtures, which consist of alkali nitrate, carbonate and sulfate systems with alkali halide systems.

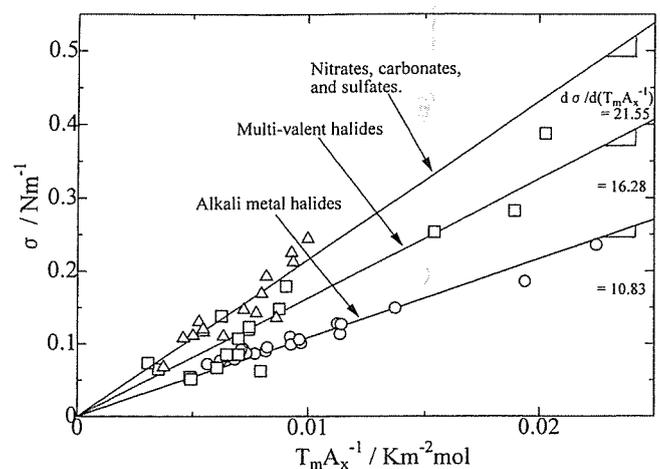


Fig. 2. Correlation of surface tension σ_x with $T_m A_x^{-1}$ for various molten salts.

Table 1. Data for the determination of β' for ionic melts.

| Element | $M/10^{-3} \text{ kg mol}^{-1}$ | T_m/K | $d/10^3 \text{ kgm}^{-3}$ | σ/Nm^{-1} | $V_x/10^{-6} \text{ m}^3 \text{ mol}^{-1}$ | $T_m A_x^{-1}/\text{Km}^{-2} \text{ mol}$ |
|-------------------------------------|---------------------------------|---------|---------------------------|-------------------------|--|---|
| Alkali Halides | | | | | | |
| LiF | 25.939 | 1121 | 1.809 | 0.2356 | 14.34 | 0.0225 |
| LiCl | 42.397 | 883 | 1.502 | 0.1274 | 28.22 | 0.0113 |
| LiBr | 86.845 | 823 | 2.529 | 0.1095 | 34.34 | 0.00923 |
| LiI | 133.85 | 742 | 3.109 | 0.09479 | 43.05 | 0.00692 |
| NaF | 41.988 | 1265 | 1.949 | 0.1859 | 21.54 | 0.0194 |
| NaCl | 58.442 | 1074 | 1.552 | 0.1140 | 37.66 | 0.0113 |
| NaBr | 102.89 | 1023 | 2.342 | 0.1007 | 43.93 | 0.00973 |
| NaI | 149.90 | 933 | 2.742 | 0.08637 | 54.67 | 0.00767 |
| KF | 58.097 | 1130 | 1.91 | 0.1442 | 30.42 | 0.0137 |
| KCl | 74.551 | 1045 | 1.527 | 0.09904 | 48.82 | 0.00927 |
| KBr | 119.00 | 1013 | 2.127 | 0.08965 | 55.95 | 0.00820 |
| KI | 166.00 | 958 | 2.448 | 0.07859 | 67.81 | 0.00682 |
| RbF | 104.47 | 1048 | 2.925 | 0.1270 | 35.71 | 0.0114 |
| RbCl | 120.92 | 988 | 2.248 | 0.09516 | 53.79 | 0.00821 |
| RbBr | 165.37 | 953 | 2.718 | 0.08735 | 60.84 | 0.00730 |
| RbI | 212.37 | 913 | 2.906 | 0.07682 | 73.08 | 0.00619 |
| CsF | 151.90 | 976 | 3.649 | 0.1074 | 41.63 | 0.00943 |
| CsCl | 168.36 | 918 | 2.792 | 0.09164 | 60.30 | 0.00707 |
| CsBr | 212.81 | 908 | 3.134 | 0.08256 | 67.90 | 0.00647 |
| CsI | 259.81 | 894 | 3.197 | 0.07212 | 81.27 | 0.00564 |
| Multi-valent Halides | | | | | | |
| MgCl ₂ | 95.200 | 987 | 1.682 | 0.06231 | 56.60 | 0.00793 |
| CaF ₂ | 78.075 | 1691 | 2.518 | 0.3871 | 31.01 | 0.0203 |
| CaCl ₂ | 110.98 | 1045 | 2.085 | 0.1478 | 53.23 | 0.00883 |
| CaBr ₂ | 199.89 | 1015 | 3.116 | 0.1196 | 64.15 | 0.00741 |
| CaI ₂ | 293.89 | 1013 | 3.439 | 0.08588 | 85.46 | 0.00618 |
| SrF ₂ | 125.60 | 1750 | 3.47 | 0.2820 | 36.20 | 0.0181 |
| BaF ₂ | 175.30 | 1563 | 4.214 | 0.2530 | 41.60 | 0.0157 |
| ZnCl ₂ | 136.30 | 591 | 2.525 | 0.05370 | 53.98 | 0.00497 |
| ZnBr ₂ | 225.20 | 675 | 3.466 | 0.05133 | 64.97 | 0.00489 |
| CdCl ₂ | 183.30 | 841 | 3.388 | 0.08495 | 54.10 | 0.00696 |
| CdBr ₂ | 272.20 | 840 | 4.076 | 0.06707 | 66.78 | 0.00603 |
| HgBr ₂ | 360.30 | 511 | 5.119 | 0.06492 | 70.38 | 0.00355 |
| PbCl ₂ | 278.10 | 772 | 4.954 | 0.1381 | 56.14 | 0.00623 |
| LaCl ₃ | 245.30 | 1128 | 3.213 | 0.1211 | 76.35 | 0.00754 |
| PrCl ₃ | 247.30 | 1058 | 3.227 | 0.1052 | 76.63 | 0.00719 |
| ZrCl ₄ | 233.00 | 710 | 1.643 | 0.07347 | 141.8 | 0.00309 |
| Nitrates, Carbonates, and Sulfates. | | | | | | |
| LiNO ₃ | 68.946 | 528 | 1.78 | 0.1159 | 38.73 | 0.00546 |
| NaNO ₃ | 84.995 | 583 | 1.906 | 0.1198 | 44.59 | 0.00549 |
| KNO ₃ | 101.10 | 610 | 1.867 | 0.1110 | 54.15 | 0.00505 |
| CsNO ₃ | 194.91 | 683 | 2.451 | 0.09176 | 79.52 | 0.00437 |
| Li ₂ CO ₃ | 73.891 | 1008 | 1.832 | 0.2437 | 40.33 | 0.0102 |
| Na ₂ CO ₃ | 105.99 | 1118 | 1.976 | 0.2124 | 53.64 | 0.00931 |
| K ₂ CO ₃ | 138.21 | 1168 | 1.895 | 0.1693 | 72.93 | 0.00792 |
| Rb ₂ CO ₃ | 230.94 | 1113 | 2.815 | 0.1504 | 82.04 | 0.00698 |
| Cs ₂ CO ₃ | 192.91 | 1065 | 3.439 | 0.1356 | 56.10 | 0.00861 |
| Li ₂ SO ₄ | 109.95 | 1132 | 2.003 | 0.2249 | 54.89 | 0.00928 |
| Na ₂ SO ₄ | 142.04 | 1163 | 2.069 | 0.1922 | 68.65 | 0.00822 |
| K ₂ SO ₄ | 174.28 | 1342 | 1.869 | 0.1425 | 93.25 | 0.00772 |
| Rb ₂ SO ₄ | 422.00 | 1323 | 2.549 | 0.1314 | 165.6 | 0.00520 |
| Cs ₂ SO ₄ | 361.87 | 1292 | 3.084 | 0.1098 | 117.3 | 0.00638 |

3 Procedure for the Calculation of the Surface Tension of Molten Salt Mixtures

The surface tension σ in Eq. (1) of molten ionic mixtures can be calculated as follows:

- (i) Inserting the values for the surface tension σ_X and molar surface area A_X of the pure liquid substances at a given temperature in Eq. (1).
- (ii) Determining the excess Gibbs energies in the bulk phase at a given temperature and composition from

thermodynamic databases, and substituting them in Eq. (1).

- (iii) 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 .
- (iv) 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 σ of the molten ionic mixtures on the left-hand side of Eq. (1).

Table 2. Estimation of β^{MIX} from $d\sigma/d(T_m A_x^{-1})$ in Fig. 2.

| | $d\sigma/d(T_m A_x^{-1})$ | Converted $d\sigma/d(\Delta H_{Eva,x} A_x^{-1})$ | β' | β^{MIX} |
|---------------------------------|---------------------------|--|----------|---------------|
| Alkali Halides | 10.83 | 0.050 | 0.94 | 1.1 |
| Multi-valent Halides | 16.28 | 0.074 | 0.93 | 1.04 |
| Nitrates, Carbonates, Sulphates | 21.55 | 0.099 | 0.90 | 1.01 |

Table 3. Values of surface tension and density of pure molten salts and excess Gibbs energy $G^{E,B}(T, N_A^B, N_B^B)$ of molten salt mixtures in the bulk phase.

| A-B System Mixtures | T/K | Surface Tension/Nm ⁻¹ | Density/ 10 ⁻³ kgm ⁻³ | $G^{E,B}(T, N_A^B, N_B^B)/J \text{ mol}^{-1}$ |
|--|------|--|--|--|
| K ₂ SO ₄ -KCl | 1200 | K ₂ SO ₄ : 0.1534 | 1.93 | $(1 + N_A^B) Y_A Y_B (2136 - 2076 Y_A)$ |
| | | KCl: 0.08707 | 1.43 | |
| Na ₂ SO ₄ -NaCl | 1173 | Na ₂ SO ₄ : 0.1916 | 2.06 | $(1 + N_A^B) Y_A Y_B (1059 + 393 Y_A)$ |
| | | NaCl: 0.1105 | 1.50 | |
| NaF-NaNO ₃ | 833 | NaF: 0.2213 | 2.23 | $N_A^B N_B^B (8069 - 7180 N_B^B)$ |
| | | NaNO ₃ : 0.1044 | 1.72 | |
| NaNO ₃ -NaCl | 743 | NaNO ₃ : 0.1100 | 1.79 | $N_A^B N_B^B (1674 - 0.596 T)$ |
| | | NaCl: 0.1378 | 1.74 | |
| Li ₂ CO ₃ -LiCl | 970 | Li ₂ CO ₃ : 0.2452 | 1.84 | $(1 + N_A^B) Y_A Y_B (-1712)$ |
| | | LiCl: 0.1216 | 1.46 | |
| K ₂ SO ₄ -Na ₂ SO ₄ | 1373 | K ₂ SO ₄ : 0.1406 | 1.86 | $N_A^B N_B^B (-4393)$ |
| | | Na ₂ SO ₄ : 0.1784 | 1.97 | |
| KNO ₃ -LiNO ₃ | 600 | KNO ₃ : 0.1133 | 1.87 | $N_A^B N_B^B (-7360 - 364 N_B^B - 1937 N_A^B N_B^B - 5.334 T)$ |
| | | LiNO ₃ : 0.1119 | 1.75 | |
| KNO ₃ -NaNO ₃ | 600 | KNO ₃ : 0.1133 | 1.87 | $N_A^B N_B^B (-1640 - 280 N_B^B)$ |
| | | NaNO ₃ : 0.1180 | 1.90 | |
| Li ₂ CO ₃ -Na ₂ CO ₃ | 1000 | Li ₂ CO ₃ : 0.2449 | 2.03 | $N_A^B N_B^B (-9900 - 2590 N_A^B + 5.600 T)$ |
| | | Na ₂ CO ₃ : 0.2202 | 1.83 | |

4 Calculated Results and Discussion

First of all, we have calculated the surface tension of molten salt mixtures in the KNO₃ - LiNO₃ system for various values of β^{MIX} . Since the molten KNO₃ - LiNO₃ system has a large negative excess Gibbs energy, this system is adequate to investigate the effect of $\beta^{MIX} = \bar{G}_X^{Ex,S}(T, N_B^S) / \bar{G}_X^{Ex,B}(T, N_B^S)$ on σ . Table 3 compiles the data on the surface tension and the density of the pure components [87NIS] and the excess Gibbs energies $G^{Ex,B}(T, N_A^B, N_B^B)$ [83Pel, 88Pel].

The partial excess Gibbs energies $\bar{G}_A^{Ex,B}(T, N_B^B)$ and $\bar{G}_B^{Ex,B}(T, N_B^B)$ can be obtained from $G^{Ex,B}(T, N_A^B, N_B^B)$ as follows [83Pel]

$$G^{Ex,B}(T, N_A^B, N_B^B) = (q_A N_A^B + a_B N_B^B) Y_A Y_B (g_0 + g_1 Y_B + g_2 Y_B^2 + \dots) \quad (9)$$

where $Y_A = q_A N_A^B / (q_A N_A^B + q_B N_B^B) = 1 - Y_B$. q_A and q_B are the number of equivalents per mole of the respective component. $N_A^B = 1 - N_B^B$. g_0, g_1 and g_2 are Gibbs energy parameters.

$$\bar{G}_A^{Ex,B}(T, N_B^B) = q_A \sum_{i=0} g_i (Y_B - i Y_A) Y_B^{i+1} \quad (10)$$

$$\bar{G}_B^{Ex,B}(T, N_B^B) = q_B Y_A^2 \sum_{i=0} g_i (i + 1) Y_B^i \quad (11)$$

In Eq. (1) d_A and d_B for alkali halides, nitrates, carbonates and sulfates are evaluated by the sums of the ionic radii of the cation plus that of the anion. The data of the ionic radii

summarized by Janz [67Janz] and Shannon [76Sha] were used to determine d_A and d_B . The radii of alkali cations and halide anions are listed in Table 4. The radii of the complex anions are obtained by the sums of the radius of O²⁻ plus the radii of C⁴⁺, S⁶⁺ or N⁵⁺, as shown in Fig. 3. The

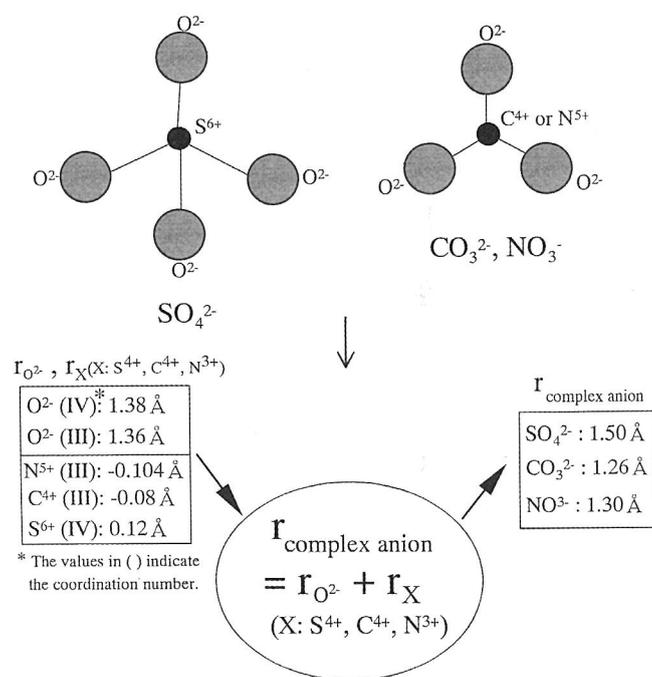


Fig. 3. Determination of r for complex anions.

Table 4. Ionic radii of alkali cations and halide anions by Janz [67Jan].

| | |
|-----------|-----------|
| Li 0.60 Å | F 1.36 Å |
| Na 0.95 Å | Cl 1.81 Å |
| K 1.33 Å | |

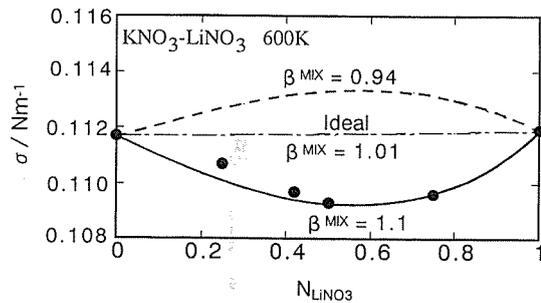


Fig. 4. Calculated results of surface tension in the $\text{KNO}_3\text{-LiNO}_3$ system for various β^{MIX} . —: Calc., ●: Exp. [87NIS].

calculated results of the surface tension σ of the molten $\text{KNO}_3\text{-LiNO}_3$ system are shown in Fig. 4. As shown in this figure, the calculated results for $\beta^{\text{MIX}} = 1.1$ agree well with the experimental values [87NIS]. When β^{MIX} is smaller than unity, the calculated results are located in the opposite areas for the experimental results across the calculated result for ideal solution. These results show that the value of β^{MIX} must be larger than unity for molten ionic mixtures. Consequently, $\beta^{\text{MIX}} = 1.1$ can be applied even to molten salt mixtures which consist of alkali ni-

trate, carbonate and sulfate systems with alkali halide systems.

Figures 5a and b show the calculated results of the surface tension of some common ion alkali halides, nitrates, carbonates and sulfates mixtures. As shown in these figures, the calculated results agree well with the experimental data [87NIS] in those mixtures. As described above, $\beta^{\text{MIX}} = 1.1$ can be applied to the common ion alkali halides, nitrates, carbonates and sulfates mixtures even though the gradient of the relation between σ_X and T_m/A_X (or σ_X and $\Delta H_{\text{Eva},X}/A_X$) for alkali nitrates, carbonates and sulfates is different from that of alkali halides as shown in Fig. 2. The former group has a larger surface tension for a given T_m/A_X than the latter ones because of the smaller value of β^{MIX} . The energy to form the relaxation structure in the surface ΔE_X is proportional to $(U_X^S - U_X^B)$, which is roughly proportional to σ_X because of $|U_X^S - U_X^B| \gg \Delta E_X$ in Eq. (5). The extent of their surface relaxation in the former group is, therefore, estimated to be larger than that of alkali halides. Thus, the value of ζ for alkali nitrates, carbonates and sulfates is supposed to be smaller than that of alkali halides, which keeps the value of β^{MIX} to be 1.1 in Eq. (8).

5 Concluding Remarks

A thermodynamic model has been derived for the surface tension of molten ionic mixtures in common ion alkali halide, nitrate, carbonate and sulfate systems considering the surface relaxation and the ionic sizes. The relation between the excess Gibbs energy in the surface and that in the bulk

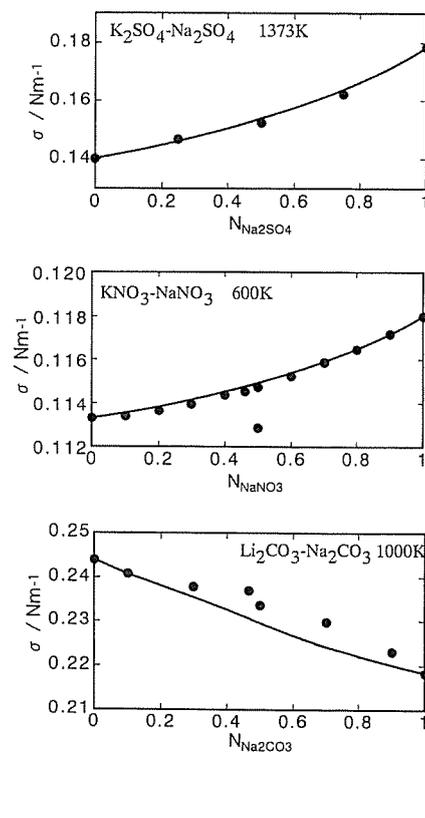


Fig. 5a. Calculated results of surface tension of molten salt mixtures in common anion systems. —: Calc., ●: Exp. [87NIS].

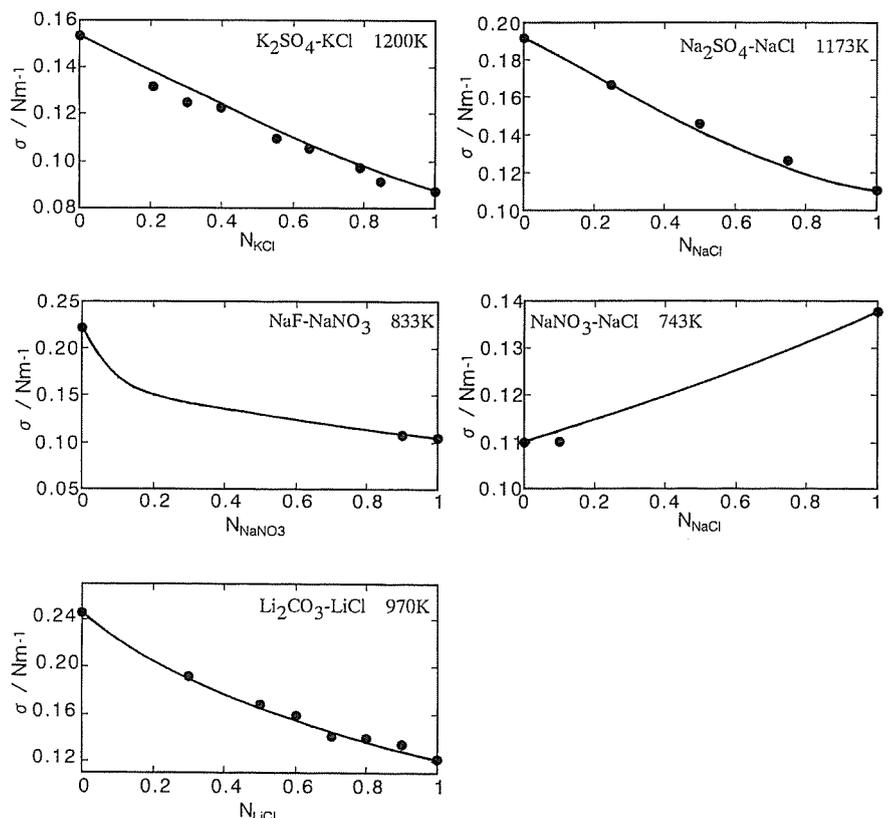


Fig. 5b. Calculated results of surface tension of molten salt mixtures in common cation systems. —: Calc., ●: Exp. [87NIS].

for alkali halide mixtures can be extended to the alkali halide, nitrate, carbonate and sulfate mixtures. 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.

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