Prediction of Surface Tension in Molten Ionic Systems

Jiayun Zhang, Qifeng Shu and Shoukun Wei

Department of Physical Chemistry,
University of Science and Technology Beijing,
Beijing 100083, China

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ABSTRACT

In this work, the so-called excess surface tension model proposed by the present authors for metallic systems has been extended and applied to molten ionic systems, slags or salts. The surface tension, σ, in a molten binary slag or salt is regarded as the summation of σ^{I} and σ^{E} to represent respectively the contributions of the linear and non-linear behaviour of the solution. The excess surface tension is correlated with mole fraction and temperature as

$$\sigma^{E} = A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2$$

where $A_j = A_{j,0} + A_{j,1}$, $j = 0, 1, 2$

The model's predicted results for some binaries of molten slags and salts, as well as for a ternary slag at a fixed mass percent ratio of two components, are provided to show the model's validity and applicability. The predicted surface tension values have been found to be in reasonable agreement with the corresponding experimental data.

I. INTRODUCTION

Surface tension is one of the most important physical properties for metallic and ionic melts involving slags and salts. Surface tension may directly affect the behaviour of bubbles or drops in gas/liquid reaction systems of materials processing, thereby influencing the rates of the relevant processes. However, the currently available surface tension data are often felt to be too few to fulfill the technological requirements either in conventional or in advanced materials processing. Furthermore, measured surface tension data in literature frequently show a considerable diversity for the same system under the same or similar experimental conditions. This situation could be caused by the high costs as well as technical difficulties in high temperature measurements. The prediction of surface tension in molten systems may reduce the amount and costs of the experimental work, which has led to a series of investigations in this direction /1-6/. A review on this topic can be found in a report by the present authors /6/. Most of the surface tension models in previous work /1-4/ dealt with metallic systems and involved some parameters depending on the structure of the liquid solutions. The authors have developed a so-called excess surface tension model /6/ using a more generalized and simple formulation to evaluate the surface tension for metallic systems. In this way, the required programming tasks and computer memories could be reduced.

In the present work, the "excess surface tension" model has been extended and applied to ionic melts, molten slags and salts. This extension would enable us to incorporate the model in a software system /7/ IDMSKM (Intellectualized Database Management System on Kinetics of Materials Processing) developed by the present research group, and, consequently, to enhance its performances of property-data retrievals for a variety of molten systems.

II. FORMULATION

A. Unaries

It has been commonly noted /3,8,9/, that the surface tension, σ, of a pure liquid can be correlated with temperature, T, by the following expression

$$\sigma = \sigma_0 + \frac{d\sigma}{dT} \bullet T \qquad (1)$$

In a moderate temperature range, usually not greater than 400 or 500°C, $\frac{d\sigma}{dT}$ can be estimated as constant, therefore Eq. (1) can be re-written as

$$\sigma = C_0 + C_1 T \qquad (2)$$

Eq. (2) is also applicable to the melt with a specified chemical composition, which has been confirmed by quite a lot of experimental studies published in literature /9/.

B. Binary systems

In the present model, the surface tension for a solution is expressed as follows:

$$\sigma = \sigma^I + \sigma^E \qquad (3)$$

and

$$\sigma^I = \sum x_i \sigma_i \qquad (4)$$

where x_i and σ_i respectively indicate the mole fraction and surface tension for pure component i. σ^I and σ^E represent the contributions of the ideal and non-ideal behaviour of the solution respectively, and σ^E in the model has been designated as the excess surface tension. The formalism for excess Gibbs energy of mixing in a binary solution by Redlich and Kister has been borrowed for the evaluation of σ^E, *i.e.*:

$$\sigma^E = x_1 x_2 [A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2] \qquad (5)$$

where A_0, A_1, A_2 are the interaction coefficients independent of composition and vary with temperature linearly as

$$A_j = A_{j,0} + A_{j,1} T, \; j = 0, 1, 2, \qquad (6)$$

$A_{j,0}$ and $A_{j,1}$ could be obtained by optimizing an appropriate amount of experimental data in a certain composition and temperature range.

III. RESULTS

Figures 1 and 2 give a comparison of model

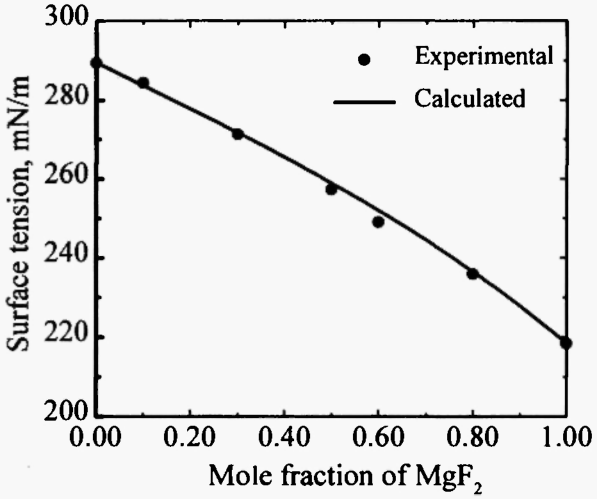

Fig. 1: A comparison between model predicted and experimental surface tension values of CaF_2-MgF_2 system at 1773K

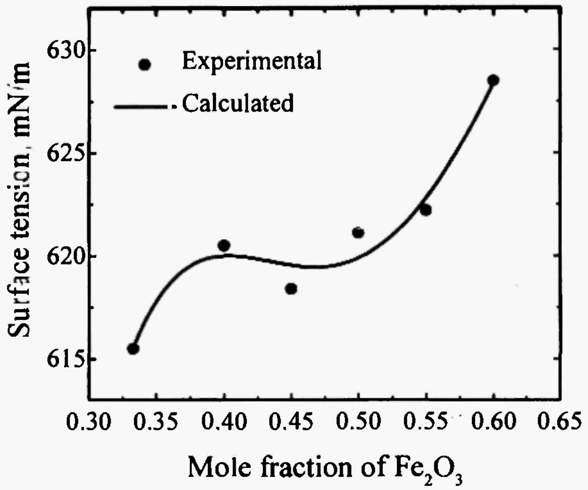

Fig. 2: A comparison between model predicted and measured surface tension data of CaO-Fe_2O_3 at 1723K

predicted results with the corresponding experimental data for CaF_2-MgF_2 /10/ and CaO-Fe_2O_3 /11/ systems respectively. Figure 3 illustrates such a comparison for Al_2O_3-SiO_2 system /12/ in a temperature range between 2273-2573K. Figure 4 is a similar comparison for a melt of Cr_2O_3-Al_2O_3 /12/, where experimental data at 2500, 2550 and 2600 K have been adopted in the optimization, while the dotted and dashed lines are extrapolated values using the optimized parameters. The model has been applied to molten oxide and salt mixtures. Figure 5 shows such an example for CaF_2-MgO system /13/ in a temperature range of 1823-1973K.

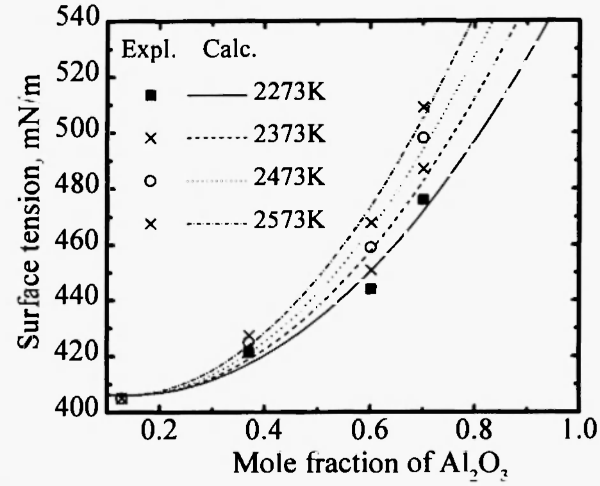

Fig. 3: A comparison between model predicted and measured surface tension data of Al_2O_3-SiO_2 system between 2273 and 2573K

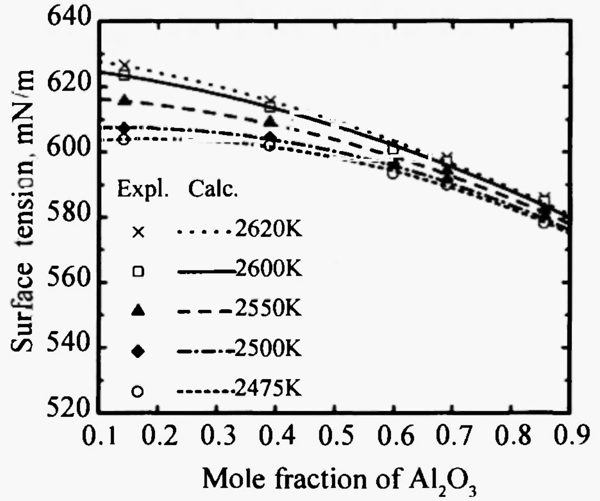

Fig. 4: A comparison between model predicted and measured surface tension data of Al_2O_3- Cr_2O_3 system between 2475 and 2620K

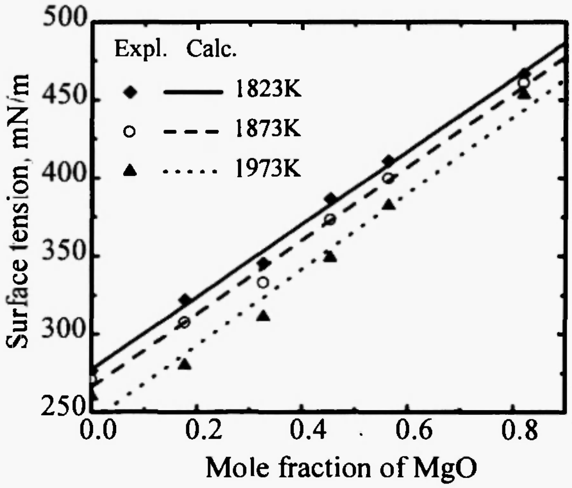

Fig. 5: A comparison between model predicted and measured surface tension data of CaF_2-MgO system between 1823 and 1973K

IV. DISCUSSION

It is noted that the excess surface tension model could fit the experimental data well for binary ionic melts, slags and salts. The model prediction can reach a reasonable accuracy as long as an appropriate amount of experimental data is available. The present model could avoid tackling problems caused by the complex structure in liquid ionic systems.

It can be seen in Figures 1-5 that the surface tension of a binary system exhibits a continuous function of mole fraction. However, two inflection points can be seen in Figure 2, which could be explained by the following statements. Combining and re-arranging Eqs. (3)-(5) lead to a polynomial function as follows:

$$\sigma = a + bx + cx^2 + dx^3 + ex^4 \qquad (7)$$

where a, b, c, d, e are constant values independent of composition at a specified temperature. If A_0, A_1, A_2 in Eq. (5) take non-zero values from the optimization, non-zero constants a, b, c, d, e will be obtained. This would result in a quaternary polynomial function as shown in Eq. (7), hence, illustrating two inflection points as shown in Figure 2. The quaternary polynomial function could be attributed to the variation of the nature of the structure in the corresponding molten system. For example, the Fe_2O_3 rich side of the phase diagram of CaO- Fe_2O_3 /14/, the liquidus temperature declines to 1473K, a minimum at the composition of the eutectic compound, $CaO{\bullet}2Fe_2O_3$ first. Then, it goes up to 1722K, a melting point of the compound ($2CaO{\bullet}2Fe_2O_3$) at the composition $x_{Fe2O3}=0.33$. A reasonable accuracy could be reached by setting A_1 and A_2 in Eq. (5) equal to zero, *i. e.* $\sigma^E = A_0 x_1 x_2$, for some binaries as shown in Figures 3 and 4. By analogy, $\sigma^E = A_0 x_1 x_2$ may imply that the melts exhibit their behaviour as regular solutions. Similarly, if A_0, A_1 and A_2 all equal zero, the solution may verify ideal behaviour, hence a linear function of mole fraction could be obtained. In Figures 1 and 5, the behaviours of the two halide-containing binaries demonstrate such a tendency. If only A_2 in Eq. (5) equals zero, σ as a ternary polynomial function of x would be obtained.

If the composition range is relatively narrow, it is a common way to correlate the surface tension with a mole fraction using a linear function. This is reasonable and recommended especially when the experimental data show a lower precision. Figure 6 is an example for the surface tension of CaO-SiO_2 /15/ system.

The motivation for introducing the so-called excess surface tension was to present the interactions between the components in a solution. For binaries, the interaction would be relatively simple, while for higher order systems interactions between more components have to be involved. In this case, Eq. (5) should be modified. This is a general way to expand the model application to more complex melts; nevertheless the model would be more complicated.

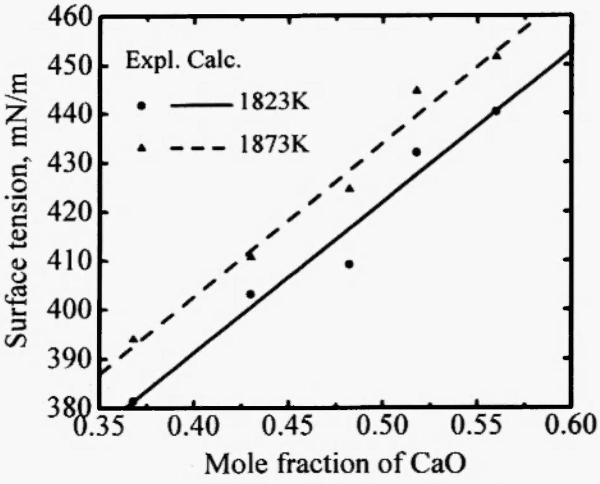

Fig. 6: An example of calculated surface tension in a small composition range of CaO-SiO_2 system using linear fitting

It is often of interest to deal with the surface tension in a ternary system when the mass percent ratio of two components is maintained constant. It could be a proper yet simple treatment to regard the system as a quasi-binary. Thus, attention could be focused on correlating the surface tension with the mole faction of the third component. Figure 7 demonstrates the variations of surface tension with mole fraction of Fe_2O_3 in CaO-Fe_2O_3-Al_2O_3 system between 1723 and 1923K, where the ratio of mass% of CaO to mass% of Al_2O_3 approximates to unity /16/.

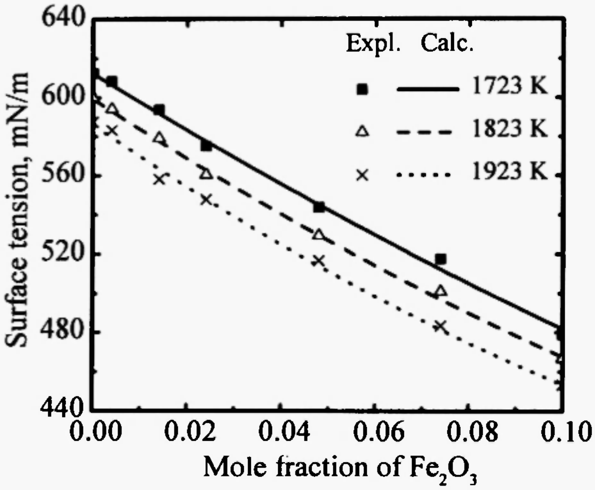

Fig. 7: Calculated surface tension variation with Fe_2O_3 in CaO-Fe_2O_3-Al_2O_3 system between 1723 and 1923 K

The excess surface tension introduced in the present model could, in a certain degree, reflect the deviation for an ionic solution with the ideal behaviour. On the other hand, the optimized parameters, $A_{j,0}$ and $A_{j,1}$, involved in the model, possess an empirical feature due to a mole fraction being used in the formulation rather than a properly expressed ionic concentration. The model modification to quantify the interactions between different ions present in a molten slag or salt would require much more information regarding the ionic structure in the molten system of interest. This would include dealing with ions present and relationship between the ion concentration with the chemical composition in molten systems. The knowledge available in this area, however, needs to be very much improved to meet such a requirement.

V. SUMMARY AND CONCLUSION

In the present model, the so-called excess surface tension has been introduced to describe the deviation of the behaviour in molten ionic systems from the ideality. By analogy, Redlich-Kister formalism for Gibbs energy of mixing in binary solutions has been borrowed to correlate the excess surface tension with mole fraction of the same. Combining the linear relationship of surface tension with temperature, the model has been used to predict the surface tension for a series of molten binary slags and salts as well as ternaries with a fixed mass percent ratio between two components. The model predicted results have shown reasonable accuracy and good agreements with the corresponding experimental data.

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