Pb-free solders: Comparison of different geometrical models in calculating of enthalpy of mixing of In-Sn-Zn ternary system

A. Boulouiz, M. El Moudane, M. Mekkaoui, A. Sabbar*

*Equipe de Physico-chimie des matériaux et nanomatériaux: Dépollution, environnement et développement durable, Université Mohammed V-Agdal, Faculté des Sciences, Av. Ibn Batouta, B.P. 1014, Rabat, Morocco

Laboratoire de Matériaux, Nanotechnologies et Environnement, Université Mohammed V-Agdal, Faculté des Sciences, Av. Ibn Batouta, B.P. 1014, Rabat, Morocco

*Corresponding author: asabbar2001@yahoo.fr (A. Sabbar) (00212661409934)

“This article is dedicated to our dear Professor Jean Pierre Bros Ex-Professor at the University of Marseille, France”

Abstract
In this paper, the general solution model of Chou has been used to predict the integral enthalpies of mixing of liquid In-Sn-Zn ternary alloys in five selected sections, \( x_{In}/x_{Sn} = 0.15/0.85, 0.34/0.66, 0.50/0.50, 0.67/0.33 \) and 0.85/0.15. The other traditional models such as Kohler, Muggianu, Toop and Hillert are also included in calculations. Comparison with literature data was done and showed reasonable agreement with Toop and Hillert asymmetric models.

Keywords: Pb-free solders; Integral enthalpy of mixing; Geometric models; In-Sn-Zn ternary system

1. Introduction
Lead-tin (Pb-Sn) solders have been used in the electronics industry as a primary method for interconnecting electronic components and sub-assemblies for several decades. The wide-spread usage of Pb-Sn solders is due primarily to the combination of low cost and convenient material properties. But, because of the toxic nature of lead, its use is restricted in many applications. So, new lead free solders are required and tin-based multicomponent materials with alloying elements as Ag, Zn, In, Bi, Sb are likely to be most promising. Interest in Sn–Zn based alloys has recently considerably increased again, mainly due to their possible application as high-temperature lead-free solders [1]. One of the concerns about Sn–Zn solders had been that they can easily corrode in high humidity which would clearly be a drawback for the reliability of corresponding solder joints. Various ternary and quaternary additions have been discussed in the past to further improve the properties of binary Sn–Zn solders, among them also the element In. McCormack and Jin [2, 3] reported that the addition of In to Sn–Zn alloys can improve the wetting characteristics of the alloys and lower their melting temperature. Recently, Rechchach et al. [4] have measured the enthalpies of mixing in the liquid ternary In–Sn–Zn alloys over the entire composition at 773 K. Generally, relatively high investigating temperatures and the evaporation of some metals could make experimental measuring difficult and expensive. That is the main reason for applying thermodynamic predicting methods.

The main purpose of this study is the calculation of the enthalpies of mixing of the liquid phase in the ternary system In-Sn-Zn at 773 K by using the ternary geometric models of Chou [5], Kohler [6], Muggianu et al. [7], Toop [8] and Hillert [9]. The calculated results are compared to the experimental one [4].

2. Literature survey
2.1. Binary In-Sn, In-Zn and Sn-Zn systems
Several calorimetric investigations of the enthalpy of mixing of liquid In-Sn alloys can be found in the literature. They cover the entire composition range and a temperature range from 521 to 1175 K [10-18]. The most recent experimental investigation of the enthalpy of mixing, using direct-reaction calorimetry at 773 K over the entire composition range, was done by Rechchach et al. [4].

The enthalpy of mixing for liquid In-Zn alloys was determined calorimetrically [19-21]. Emf methods were applied to derive the corresponding values [22-24]. All experimental data show positive values for the enthalpy
of mixing. Lee [25] presented a thermodynamic assessment based on the above-mentioned experimental data [19-24]. The calculated and experimental results were in good agreement.

Several calorimetric investigations of the enthalpy of mixing of Sn-Zn liquid alloys at different temperatures are available in the literature [26-30]. Other authors [31-34] have used emf method for this purpose. All experimental data show positive values for the enthalpy of mixing of liquid Sn-Zn alloys. A thermodynamic assessment of the enthalpy of mixing of liquid Sn-Zn alloys were reported [25, 35, 36].

2.2. Ternary In-Sn-Zn system

Enthalpies of mixing of liquid In-Sn-Zn alloys have already been measured by several authors using direct reaction calorimetry [37, 38]. Cui et al. [39], using CALPHAD-type approach have calculated the partial enthalpies of mixing of In, Sn and Zn. Xie et al. [40] used a similar approach for a thermodynamic assessment of the In-Sn-Zn ternary system based on a rather limited number of literature data and observed good agreement with the literature. Recently, Rechchach et al. [4], using a Calvet-type microcalorimeter and a drop calorimetric technique, have measured the partial and the integral enthalpies of mixing of liquid ternary In-Sn-Zn alloys at 773 K along seven sections and over a large composition range. The ternary data of the authors were fitted using the well known Redlich-Kister-Muggianu equation.

3. Theoretical fundamentals

In this work, the investigated system is considered in the order 1-2-3 related to In-Sn-Zn.

3.1 A general solution model of Chou [5]

The method provided by Chou [5] has been proved to be the most reasonable one in all aspects among current geometrical models. This model can not only generalize various kinds of situations, break down the boundary between symmetrical and asymmetrical systems, but can also thoroughly rule out any human interference in the calculation process. The correctness of this model has already been proved theoretically and the accuracy of calculation has also been shown in some practical examples [41, 42]. This model is applied for calculating the enthalpy of mixing of the In-Sn-Zn ternary system.

To apply the Chou’s model to the In-Sn-Zn ternary system, it is necessary to calculate the similarity coefficients $\xi_{ij}$ for three binaries which are defined by $\eta_i$ called the deviation sum of squares:

$$\xi_{12} = \frac{\eta_1}{\eta_1 + \eta_{II}}$$  \hspace{1cm} (1)

$$\xi_{23} = \frac{\eta_{II}}{\eta_{II} + \eta_{III}}$$  \hspace{1cm} (2)

Where

$$\eta_1 = \frac{1}{0} \int \left( \Delta_{Mix} H_{12} - \Delta_{Mix} H_{13} \right)^2 dX_1 \hspace{1cm} (4)$$

$$\eta_{II} = \frac{1}{0} \int \left( \Delta_{Mix} H_{21} - \Delta_{Mix} H_{23} \right)^2 dX_2 \hspace{1cm} (5)$$

$$\eta_{III} = \frac{1}{0} \int \left( \Delta_{Mix} H_{31} - \Delta_{Mix} H_{32} \right)^2 dX_3 \hspace{1cm} (6)$$

and

$$X_{1(12)} = x_1 + x_3\xi_{12} \hspace{1cm} (7)$$

$$X_{2(23)} = x_2 + x_1\xi_{23} \hspace{1cm} (8)$$

$$X_{3(31)} = x_3 + x_2\xi_{31} \hspace{1cm} (9)$$

The basic equation of the general solution model, derived by Chou, is given as follows:

$$\Delta_{Mix} H_{123} = x_1 x_2 x_3 \sum_v A_{12}^v (x_1 - x_2)^v + x_2 x_3 \sum_v A_{23}^v (x_2 - x_3)^v + x_3 x_1 \sum_v A_{31}^v (x_3 - x_1)^v + x_1 x_2 x_3 f$$  \hspace{1cm} (10)

$\Delta_{Mix} H_{123}$ is an integral enthalpy of mixing for a ternary 1-2-3 system, $x_1$, $x_2$, $x_3$ are the mole fractions of ternary alloy, $A_{ij}^v$ are parameters for binary “ij” independent of composition, only relying on temperature, which have been used in the regular type equation:

$$\Delta_{Mix} H_{ij} = X_i X_j \sum_v A_{ij}^v (X_i - X_j)^v$$  \hspace{1cm} (11)

$X_i$ and $X_j$ indicate the mole fraction of component “i” and “j” in “ij” binary system. The function $f$ is the ternary interaction coefficient expressed by:

$$f = (2\xi_{12} - 1) \left[ A_{12}^{\xi_{12}} ((2\xi_{12} - 1)x_3 + 2(x_1 - x_2)) + A_{12}^{\xi_{12}} \right] + (2\xi_{23} - 1) \left[ A_{23}^{\xi_{23}} ((2\xi_{23} - 1)x_1 + 2(x_2 - x_3)) + A_{23}^{\xi_{23}} \right] + (2\xi_{31} - 1) \left[ A_{31}^{\xi_{31}} ((2\xi_{31} - 1)x_2 + 2(x_3 - x_1)) + A_{31}^{\xi_{31}} \right]$$  \hspace{1cm} (12)
3.2. A traditional Kohler [6], Muggianu et al. [7], Toop [8] and Hillert [9] models

There are several traditional models used to extrapolate the ternary thermodynamic properties based on the three constitutive binary systems. According to Hillert [9], the four traditional models [6-9], generally used due to their simplicity, are classified into two categories: symmetrical (Kohler and Muggianu models) and asymmetrical (Toop and Hillert models). The use of a symmetrical model when an asymmetrical model is more appropriate can often give rise to errors.

The four different extrapolation models [6-9] were used to calculate the enthalpy of mixing in the ternary In-Sn-Zn system which contains three binary systems, and the information of all these binary systems should be known before using the models.

The various predictive extensions from the binary to ternary systems are shown below.

**Kohler model [6]:**

\[
\Delta_{\text{Mix}} H_{123} = (x_1 + x_2)^2 \Delta_{\text{mix}} H_{12} \left( \frac{x_1}{x_1 + x_2}; \frac{x_2}{x_1 + x_2} \right) + (x_1 + x_3)^2 \Delta_{\text{mix}} H_{13} \left( \frac{x_1}{x_1 + x_3}; \frac{x_3}{x_1 + x_3} \right) + (x_2 + x_3)^2 \Delta_{\text{mix}} H_{23} \left( \frac{x_2}{x_2 + x_3}; \frac{x_3}{x_2 + x_3} \right)
\]

\[(13)\]

**Muggianu et al. Model [7]:**

\[
\Delta_{\text{Mix}} H_{123} = \frac{4x_1 x_2}{(1 + x_1 - x_2)(1 + x_2 - x_1)} \Delta_{\text{mix}} H_{12} \left( \frac{1 + x_1 - x_2}{2}; \frac{1 + x_2 - x_1}{2} \right) + \frac{4x_1 x_3}{(1 + x_1 - x_2)(1 + x_3 - x_1)} \Delta_{\text{mix}} H_{13} \left( \frac{1 + x_1 - x_3}{2}; \frac{1 + x_3 - x_1}{2} \right) + \frac{4x_2 x_3}{(1 + x_2 - x_3)(1 + x_3 - x_2)} \Delta_{\text{mix}} H_{23} \left( \frac{1 + x_2 - x_3}{2}; \frac{1 + x_3 - x_2}{2} \right)
\]

\[(14)\]

**Toop model [8]:**

\[
\Delta_{\text{Mix}} H_{123} = (x_1 + x_2)^2 \Delta_{\text{mix}} H_{12} \left( \frac{x_1}{x_1 + x_2}; \frac{x_2}{x_1 + x_2} \right) + \frac{x_2}{(1 - x_3)} \Delta_{\text{mix}} H_{23} (1 - x_3; x_3)
\]

\[(15)\]

**Hillert model [9]:**

\[
\Delta_{\text{Mix}} H_{123} = \frac{x_1 x_2}{\nu_{12} v_{21}} \Delta_{\text{mix}} H_{12} (\nu_{12}; v_{21}) + \frac{x_2}{(1 - x_3)} \Delta_{\text{mix}} H_{23} (1 - x_3; x_3)
\]

\[(16)\]

Where \(\nu_{12} = \frac{1 + x_1 - x_2}{2}; v_{21} = \frac{1 + x_2 - x_1}{2}\)

For the calculation of integral enthalpies of mixing of ternary solution according to the Toop [8] and Hillert [9] asymmetrical models one of the three elements has to be chosen as a symmetric component.

4. Results of calculation and discussion

The calculations in the investigated ternary system In-Sn-Zn were carried out along the lines of a constant \(x_{Sn}/x_{Zn}\). The five selected cross sections are given in Table 1.

**Table 1.** The five investigated sections

<table>
<thead>
<tr>
<th>Section</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>(x_{Sn}/x_{Zn})</td>
<td>0.15/0.85</td>
<td>0.34/0.66</td>
<td>0.50/0.50</td>
<td>0.67/0.33</td>
<td>0.85/0.15</td>
</tr>
</tbody>
</table>

The integral enthalpies of mixing of the three binary systems are taken from Rechchach et al.[4] for In-Sn system at 773 K and from Hultgreen et al.[14] for In-Zn and Sn-Zn systems at 700 and 750 K respectively. Binary regular-solution parameters \(A_{ij}^v\) (Eq. (11)) for the binary systems In-Sn, In-Zn and Sn-Zn, used in the calculations are shown in Table 2. It should be noted that:

\(\Delta_{\text{Mix}} H_{ij} = \Delta_{\text{Mix}} H_{ji}, A_{ij}^v = A_{ji}^v\), when \(v\) is even and \(A_{ij}^v = -A_{ji}^v\), when \(v\) is odd.

**Table 2.** Binary interaction parameters of the integral enthalpy of mixing.

<table>
<thead>
<tr>
<th>Binary system</th>
<th>(A_{ij}^v) (J/mol)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-Sn</td>
<td>(A_{\text{InSn}}^0 = -1488, A_{\text{SnIn}}^1 = -1041)</td>
<td>[4]</td>
</tr>
<tr>
<td>In-Zn</td>
<td>(A_{\text{InZn}}^0 = 13095, A_{\text{ZnIn}}^1 = -2682)</td>
<td>[14]</td>
</tr>
<tr>
<td>Sn-Zn</td>
<td>(A_{\text{SnZn}}^0 = 12728, A_{\text{ZnSn}}^1 = -5074)</td>
<td>[14]</td>
</tr>
</tbody>
</table>
The plots of integral enthalpies of mixing for the three binary systems at 773 K are shown in Figure 1.

![Figure 1 Integral enthalpies of mixing in the liquid In-Sn (773 K), In-Zn (700 K) and Sn-Zn (750 K) binary systems (Standard states: pure liquid metals).](image-url)

The enthalpies of mixing are endothermic for In-Zn and Sn-Zn systems with a maximum of about 3200 J/mol at \( x_{Zn} = 0.60 \), whereas the In-Sn system has a slight exothermic behaviour with a minimum of -400 J/mol at \( x_{In} = 0.58 \). According to these results, one can conclude that this ternary system should be regarded as an asymmetrical system. The calculated results predicted by Toop or Hillert asymmetric model will be better than those from the Kohler or Muggianu symmetrical model. It has to be mentioned here that, the arrangement of three components to a triangle for an asymmetrical model is very important, because a wrong arrangement will lead to an even worse result than a symmetrical model. In this example, the component “Zn” has been selected as a symmetric point.

Using the Equations (1) to (6) developed by Chou, the deviation sum of squares and the similarity coefficients for the three binaries In–Sn, Sn–Zn and Zn–In are listed in Table 3.

**Table 3. Deviation sum squares and similarity coefficients for Chou’s model [5] applied on In-Sn-Zn**

<table>
<thead>
<tr>
<th>Deviation sum of squares (J/mol²)</th>
<th>( \eta_I = 7101619.54 )</th>
<th>( \eta_{II} = 6914551.51 )</th>
<th>( \eta_{III} = 31735.65 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interaction of</td>
<td>In-Sn</td>
<td>In-Zn</td>
<td>Sn-In</td>
</tr>
<tr>
<td>Similarity coefficients</td>
<td>( \xi_{Sn-Sn} = 0.5067 )</td>
<td>( \xi_{Sn-Zn} = 0.9954 )</td>
<td>( \xi_{Zn-In} = 0.0045 )</td>
</tr>
</tbody>
</table>

From these resulting values (Table 3), one can conclude that the integral enthalpies of mixing of In-Zn and Sn-Zn are more similar to each other than to In-Sn, respectively. These \( \xi \)-values indicate also that this system is an asymmetrical system. In fact, Chou [5] has reported that the three similarity coefficients are not independent. Combining Eqs. (1) to (3) and eliminating \( \eta_I, \eta_{II}, \eta_{III} \) the following relation is obtained:

\[
(1 - \xi_{InSn})(1 - \xi_{SnZn})(1 - \xi_{ZnIn}) = \xi_{InSn} \xi_{SnZn} \xi_{ZnIn} \tag{17}
\]
In order to check the correction of calculated $\xi$, the Eq. (17) has been used:

$$\left(1 - \xi_{\text{InSn}}\right)\left(1 - \xi_{\text{SnZn}}\right)\left(1 - \xi_{\text{ZnIn}}\right) = \xi_{\text{InSn}} \xi_{\text{SnZn}} \xi_{\text{ZnIn}} = 0.00227$$  \hspace{1cm} (18)

According to Eq. (17) and reference [5], the above result shows that the calculations of $\xi$ are correct. From Eq. (17), it may be seen that, if any one of the three similarity coefficients approaches zero, then there must be one similarity coefficient which approaches unity. This situation, obtained in this work for our investigated In-Sn-Zn system, represents the common feature of the asymmetrical Toop and Hillert models. Based on these data, ternary interaction coefficients $f$ which enabled determination of integral enthalpies of mixing were calculated according to Eq. (12) for all investigated cross sections in the In-Sn-Zn ternary system, and are given in Table 4.

**Table 4.** Ternary interaction coefficients, $f$ calculated according to Eq. (12) for the In-Sn-Zn system at 773 K (in J/mol)

<table>
<thead>
<tr>
<th>Mole fraction $x_{\text{Zn}}$</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>-6303</td>
<td>-6069</td>
<td>-5872</td>
<td>-5662</td>
<td>-5441</td>
</tr>
<tr>
<td>0.1</td>
<td>-6686</td>
<td>-6475</td>
<td>-6298</td>
<td>-6110</td>
<td>-5910</td>
</tr>
<tr>
<td>0.2</td>
<td>-7069</td>
<td>-6882</td>
<td>-6724</td>
<td>-6557</td>
<td>-6380</td>
</tr>
<tr>
<td>0.3</td>
<td>-7452</td>
<td>-7288</td>
<td>-7151</td>
<td>-7004</td>
<td>-6849</td>
</tr>
<tr>
<td>0.4</td>
<td>-7835</td>
<td>-7695</td>
<td>-7577</td>
<td>-7451</td>
<td>-7318</td>
</tr>
<tr>
<td>0.5</td>
<td>-8219</td>
<td>-8102</td>
<td>-8003</td>
<td>-7899</td>
<td>-7788</td>
</tr>
<tr>
<td>0.6</td>
<td>-8602</td>
<td>-8508</td>
<td>-8430</td>
<td>-8346</td>
<td>-8257</td>
</tr>
<tr>
<td>0.7</td>
<td>-8985</td>
<td>-8915</td>
<td>-8856</td>
<td>-8793</td>
<td>-8727</td>
</tr>
<tr>
<td>0.8</td>
<td>-9368</td>
<td>-9322</td>
<td>-9282</td>
<td>-9240</td>
<td>-9196</td>
</tr>
<tr>
<td>0.9</td>
<td>-9752</td>
<td>-9728</td>
<td>-9708</td>
<td>-9688</td>
<td>-9665</td>
</tr>
<tr>
<td>1</td>
<td>-10135</td>
<td>-10135</td>
<td>-10135</td>
<td>-10135</td>
<td>-10135</td>
</tr>
</tbody>
</table>

The calculated results for the five models in the ternary investigated sections (A-E) are listed in Table 5. The experimental results [4] are also included for comparison. Based on the all calculated results shown in Figure 2, it could be concluded that the comparison between calculated results indicate that the good agreement is obtained between Chou, Toop and Hillert model. In addition, the results obtained by the Toop model show the best agreement with the experimental results. Additionally, if one takes the root mean square deviation corresponding to experimental results for each traditional model, i.e.

$$S = \frac{1}{N} \sum_{i=1}^{N} \left(\Delta_{\text{Mix}}H_{\text{the},i} - \Delta_{\text{Mix}}H_{\text{exp},i}\right)^2$$  \hspace{1cm} (18)

Where $\Delta_{\text{Mix}}H_{\text{the},i}$ and $\Delta_{\text{Mix}}H_{\text{exp},i}$ represent the integral enthalpies of mixing at a fixed composition “i” for a theoretical model and an experimental results, respectively, while $N$ is the total number of investigated alloys. According to the calculation, these S for Toop, Hillert, Chou, Muggianu, and Kohler models are 12.55, 12.79, 12.93, 32.99 and 37.57, respectively. From these S-values, Toop and Hillert asymetric models give the minimum value (12.55 and 12.79 respectively).

**Table 5.** Integral enthalpies of mixing of In-Sn-Zn system at 773 K calculated by different predicting models and measured by Rechchach et al. [4].

<table>
<thead>
<tr>
<th>Mole fraction $x_{\text{Zn}}$</th>
<th>Kohler</th>
<th>Muggianu</th>
<th>Chou</th>
<th>Toop</th>
<th>Hillert</th>
<th>Exp. [4]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>-97</td>
<td>-97</td>
<td>-97</td>
<td>-97</td>
<td>-97</td>
<td>-97</td>
</tr>
<tr>
<td>0.1</td>
<td>766</td>
<td>803</td>
<td>734</td>
<td>741</td>
<td>733</td>
<td>750</td>
</tr>
<tr>
<td>0.2</td>
<td>1620</td>
<td>1641</td>
<td>1526</td>
<td>1537</td>
<td>1525</td>
<td>1533</td>
</tr>
<tr>
<td>0.3</td>
<td>2382</td>
<td>2368</td>
<td>2229</td>
<td>2241</td>
<td>2228</td>
<td>2215</td>
</tr>
<tr>
<td>0.4</td>
<td>2980</td>
<td>2933</td>
<td>2790</td>
<td>2802</td>
<td>2788</td>
<td>2753</td>
</tr>
<tr>
<td>0.5</td>
<td>3352</td>
<td>3285</td>
<td>3154</td>
<td>3165</td>
<td>3153</td>
<td>3100</td>
</tr>
<tr>
<td>0.6</td>
<td>3441</td>
<td>3371</td>
<td>3266</td>
<td>3274</td>
<td>3265</td>
<td>3205</td>
</tr>
</tbody>
</table>
Therefore, according to the S-values, one can confirm that the results obtained by Toop model are close to the experimental one and the investigated In-Sn-Zn system is an asymmetric system.
Conclusion
The integral enthalpies of mixing of the ternary In-Sn-Zn system were calculated by using the Chou, Kohler, Muggianu, Toop and Hillert models and compared with the experimental results. Among all the traditional predicting models, it can be concluded that Toop and Hillert models show the best agreement with the experimental data. This conclusion can be explained by the fact that the asymmetric models are the closest to the obtained geometric interpretation for the In-Sn-Zn system.
Acknowledgements—The authors are grateful to Mrs. J. El Mendili, Biostatistics Engineer, for her assistance for the calculations.

References

(2014) ; http://www.jmaterenvironsci.com/