Assessment of Surface Tension and Viscosity of In-Zn melt

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Abstract: A comparative study of the concentration dependence of surface tension and viscosity of molten In-Zn alloys at 700 K has been performed using energetics, obtained from thermodynamic analysis in the framework of self-association model. The surface tension of the alloys has been calculated from the two methods, layered structure approach and self associating mixture method, and viscosity from Moelwyn-Hughes equation and Kaptay equation. The theoretically computed results for the thermodynamic properties of the alloys are found in excellent agreement with the corresponding experimental results showing that the alloy is segregating in nature. Both surface tension and viscosity of the In-Zn alloy are found to increase with the addition of Zn atoms.

Keywords: Enthalpy of mixing; Self association; Surface tension; Viscosity.

1. INTRODUCTION

Indium, relatively rare but versatile metal, can be alloyed to many metals such as bismuth, lead, gold, platinum, gallium, tellurium, thallium, silver, tin and has been called vitamin in alloys. It can form fusible alloys with gallium, zinc etc. and are used for solders. Of many indium based alloys, In-Zn alloys in the liquid state, in particular possess several interesting features. It is reported that In-Zn alloy is eutectic in the range from 2.06 to 3.80 atomic percent of zinc having a eutectic temperature of 143.5°C [1]. The observed data of the free energy of mixing and the entropy of mixing of In-Zn alloy at 700 K [2] show remarkable deviations from the ideal values. Also the concentration fluctuation in long range limit, SCC(0) computed from observed activity data [2] shows asymmetrical behaviour about the equi-atomic composition. With these features as such the In-Zn alloy is drawing attention of the researchers [1, 3] towards the investigation of its alloying nature.

The solubility in a binary alloy can be discussed in terms of the atomic volume ratio, valence ratio and electronegativity difference of the component metals and but these factors are not explicitly available in any simple way. In order to understand the alloying behaviour of binary liquid alloys in detail, thermo-physical properties such as thermodynamic, surface and transport properties of mixing are taken into account. The energetics in a liquid alloy is comprehended from the estimation of the free energy of mixing, heat of mixing and entropy of mixing. The nature of atomic bonding resulting in a particular kind of arrangement of atoms in the alloy, either ordering or segregating, is judged from the analysis of the structural properties, the concentration fluctuation in long range limit and short range order parameter. The mechanism behind various phenomena such as mechanical behaviour, kinetics of phase transformation and catalytic activity can be understood from the knowledge of surface concentration and surface tension. Viscosity is one of the transport properties, which is required to understand the high temperature dynamics in the liquid alloys.

In the present work, we intend to carry out a theoretical study of mixing behaviour of In-Zn alloy at 700 K by computing the energetics in it from thermodynamic analysis based on self association model, and the surface tension and viscosity from the methods based on statistical thermodynamics. We employ self association model for the study of the thermodynamic properties of the alloy because the values of experimental SCC(0) are found to be greater than the ideal SCC(0) at all compositions. In computation of both surface tension and viscosity in this work, we employ the energetics like interaction energy, enthalpy of mixing etc. computed from self-association model [4-6]. Due to scanty of experimental data of surface tension and viscosity as function of composition, we intend to carry out comparative analyses for both of these properties. The surface tension is computed from layered structure approach [7-10] and
self associating mixture method [11]. For the calculation of viscosity of the alloy, we employ Moelwyn-Hughes (M-H) equation [12] and Kaptay equation [12]. In the following section, the expressions required for the calculations are presented. Section 3 outlines the results and discussion of the work, and conclusion is given in section 4.

2. THEORETICAL BASIS

2.1 Thermodynamic properties

The self-association model [4, 5] is a statistical mechanical formulation for studying phase segregating binary liquid alloys. According to this model, one mole of a binary liquid alloy A-B is assumed to consist of $N_A (= Nc_A)$ atoms of elemental metal A and $N_B (= Nc_B)$ atoms of elemental metal B situated at equivalent sites, $N$ being the total number of atoms, and $c_A$ and $c_B$ the mole fraction concentrations of A and B respectively. There is short ranged atomic interaction between the nearest neighbours that forms a polyatomic matrix leading to the formation of like atom clusters or self-associates of the type $iA$ and $jB$, where $i$ and $j$ are the numbers of atoms in the clusters of elements A and B respectively [5]. In the framework of self association model, the following expressions are used in computing the thermodynamic functions of binary liquid alloys [5]:

(i) Free energy of mixing, $G_M$

The free energy of mixing, $G_M$ is given by

$$G_M = RT \left[ c_A \ln \phi + c_B \ln (1-\phi) \right] + c_A(1-\phi)W$$

with $\phi = c_A \left( c_A + n c_B \right)$

(ii) Entropy of mixing, $S_M$

The entropy of mixing, $S_M$ is obtained by the temperature derivative of the free energy of mixing and can be put in the form

$$S_M = -R \left[ c_A \ln \phi + c_B \ln (1-\phi) \right] - c_A(1-\phi) \frac{\partial W}{\partial T}$$

(iii) Enthalpy of mixing, $H_M$

The enthalpy of mixing, $H_M$ is related to the free energy of mixing, $G_M$ and the entropy of mixing, $S_M$ by the standard thermodynamic relation

$$H_M = G_M + TS_M$$

or

$$H_M = c_A(1-\phi) \left[ W - T \frac{\partial W}{\partial T} \right]$$

2.2. Surface Properties

(i) The first approach [7, 8] links surface tension of a binary liquid alloy, $\sigma$ to its bulk thermodynamic properties through the surface tension $\sigma_A$ and $\sigma_B$, and activity coefficients $\gamma_A^*$ and $\gamma_B^*$ of the components A and B of the alloy, which can be expressed as:

$$\sigma = \sigma_A + Y \ln \frac{c_A^s}{\gamma_A^* c_A} + \frac{[p(c_A^s)^2 + q(c_A^s)]}{\alpha} \frac{W}{\alpha}$$

$$\sigma = \sigma_B + Y \ln \frac{c_B^s}{\gamma_B^* c_B} + \frac{[p(c_B^s)^2 + q(c_B^s)]}{\alpha} \frac{W}{\alpha}$$

with $Y = k_B T / \alpha$, where $k_B$ is Boltzmann constant; $p$ and $q$ are surface coordination fractions which are taken as $p = 0.5$ and $q = 0.3$ for closed packed structure; $c_A^s$ and $c_B^s$ are surface concentrations of A and B components respectively. $W$ is the order energy parameter which, in this analysis, is taken from thermodynamic calculation done in the framework of self-association model. $\alpha$ is the mean atomic surface area of the alloy which is calculated as:

$$\alpha = \sum c_k \alpha_k$$

where the atomic area of hypothetical surface for each component is calculated as:

$$\alpha_k = 1.102 \left( \frac{V_k}{N_A} \right)^{2/3}$$

where $N_A$ is Avogadro number and $V_k$ is the molar volume of the component k at the temperature of investigation, $T$, which is calculated from density of the metal at that temperature.

(ii) The second approach for computing surface properties is self-associating mixture method developed for segregating alloys. In this method the surface concentration is computed by simultaneously solving the following pair of equations [9] at all bulk concentrations and then the surface tension of the alloys is computed from either of the equations:

$$\sigma = \sigma_A + (k_B T / \alpha) \left[ \ln \frac{c_A^s}{c_A^*} \right] + p \left[ \ln \left( \frac{c_A^s}{\phi} / c_A^* \phi \right) \right] + \left( c_A^s \phi - c_A^* \phi \right) / c_A^*$$

$$+ q \left[ \ln \left( \frac{c_A^s}{\phi} \right) / \left( \phi - c_A^* \phi \right) / c_A^* \right] + i \omega / k_B T \left( \rho (1 - \phi)^2 + (q - 1)(1 - \phi)^2 \right)$$
\[ \sigma = \sigma_B + \left( k_B T / \alpha \right) \left[ \ln c_B^n / c_B^m \right] + p \left[ \ln c_B \left( 1 - \phi \right) \right] / c_B \left( 1 - \phi \right) \\
+ \left( f / j \right) \left[ (\phi - \phi) / f \right] - q \left[ \ln \left( 1 - \phi \right) / c_B + \phi \left( i - j \right) / i \right] \\
+ j \omega / k_B T \left[ \phi \left( \phi \right)^2 + (q - 1) \phi^2 \right] \] (8b)

with \( \phi = \tilde{c}_A \left( \tilde{c}_A + \tilde{c}_B \right) \) and \( \phi = \tilde{c}_A \left( \tilde{c}_A + \tilde{c}_B \right) \) (9)

where \( i \) atoms of element A (=In) are assumed to be associated with \( j \) atoms of element B (=Zn) and all other symbols have the same meanings as those in the first approach.

### 2.3. Viscosity

(i) The first equation we employ for the computation of viscosity of liquid In-Zn alloys is Moelwyn-Hughes (M-H) equation which is based on fact that the viscous flow becomes more difficult when the cohesion energy of the alloy is increased and at a temperature \( T \), it is given as [12]:

\[ \eta = \left( c_i \eta_i + c_k \eta_k \right) \left( 1 - 2c_k c_i H_m / RT \right) \] (10)

where \( \eta \) and \( \eta_k \) represent respectively the viscosity of the alloy and of pure metal \( k = A, B \); \( c_k \) the mole fraction of component \( k \), \( H_m \) the heat of mixing of the alloy and \( R \) is the universal gas constant. For most metals the variation of viscosity, \( \eta_k \) with temperature \( T \) may be expressed as [13]:

\[ \eta_k = \eta_{k0} \exp \left( E / RT \right) \] (11)

where, \( \eta_{k0} \) and \( E \) are constants for pure metal and are expressed in units of viscosity and energy per mole respectively.

(ii) The second equation that we employ to compute the viscosity of the alloys is the Kaptay equation [12]. This equation presents the theoretical relationship between the cohesion energy of the alloy and the activation energy of viscous flow. It is expressed as:

\[ \eta = h N_A \left( c_A V_A + c_B V_B + V^e \right) \exp \left( c_A G_A^* + c_B G_B^* - \alpha H_m \right) / RT \] (12)

where \( G_k^* \) is the Gibbs energy of activation of the viscous flow in pure component \( k \), given by

\[ G_k^* = RT \ln \left( \eta_k V_k \right) / h N_A \] (13)

Here, \( H_m \) is enthalpy of mixing of the alloy; \( N_A \) is Avogadro number; \( V_k \) represents the molar volumes of the component \( k \); \( V^e \) is the excess molar volume which can be neglected for simplicity [12].

### 3. RESULTS AND DISCUSSION

#### 3.1. Thermodynamic properties

At a given temperature mixing properties of a binary liquid alloy vary with the composition of the alloy. The ratio of self-associates, \( n \) and the ordering energy, \( W \) of self association model have been estimated as model fit parameters for the liquid In-Zn alloys at 700 K by using the experimental values of the free energy of mixing, \( G_m \) [2] in Eqs. (1). We have obtained the best fit values of the parameters to be \( n = 1.68 \) and \( W = +1.44 RT \). The positive sign of \( W \) indicates a tendency of like atom pairing in the liquid In-Zn alloys.

Next we have computed the entropy of mixing, \( S_m \) from Eq. (3) by estimating the temperature dependence of the energy parameter to be given as, \( \frac{\partial W}{\partial T} = -2.993 R \). The non-zero value of this term indicates that the interaction energy is temperature dependent. Using the calculated values of the free energy of mixing and the entropy of mixing, we have next computed the enthalpy of mixing, \( H_m \) of the alloy throughout the whole range of bulk concentration from Eq. (4). The enthalpy of mixing contains information about the nature of binding in the liquid alloys. Similarly, entropy of mixing helps to draw important structural information of binary liquid alloys. It represents the sharing of energy between the species in the alloys and determines the equilibrium state of the mixture.

![Figure 1- Free energy of mixing (G_m), entropy of mixing (S_m) and enthalpy of mixing (H_m) of In-Zn alloy at 700K versus concentration of Zn: solid curve-theory; circles-experimental [2].](image-url)

Theoretically computed results for \( G_m \), \( S_m \) and \( H_m \) are compared with the corresponding experimental results [2]...
in Fig. 1. The plot shows that the computed results for GM and SM are in well agreement with the experimental results but a slight departure is observed in HM. This disparity may be due to entropic contribution. The self association model thus well explains the observed thermodynamic properties of liquid In-Zn alloy at 700 K. Positive sign of the enthalpy of mixing along with the parameter W indicates that the liquid In-Zn alloy at 700 K is segregating in nature.

3.2. Surface tension

Following the reference [13], the molar volume and surface tensions of In and Zn metals at 700 K are computed. Using the value of W and the activity coefficients of the metals [2] as inputs, the surface concentration and surface tension of the liquid In-Zn alloy at 700 K have been computed by solving the pairs of equations (5a) and (5b) in the full range of bulk concentration. Next, Eqs. (7a) and (7b) are solved together for the surface concentration by assuming the liquid In-Zn alloy at 700 K to be a self-associating mixture with i=1.68 (In) and j= 1(Zn) in the ratio of self-associates and the surface tension of the alloy is computed at all bulk concentrations from either equation.

3.3. Viscosity

Using viscosities of the components from reference [13] and enthalpy of mixing computed from self association model, the viscosity of the In-Zn alloy at 700 K is calculated from Eqs. (10) and (12) as function of bulk concentrations of Zn atoms. The contribution of excess volume of the alloy, V^E is too small to be neglected and it is not taken in this work. The viscosity of the In-Zn alloy in our analysis has been found to increase with the addition of the Zn atoms. A reasonably good agreement is noticed in the sets viscosity values [Fig. 3] computed from two methods.

Figure 3- Viscosity of In-Zn alloy at 700K versus concentration of Zn: solid curve- Moelwyn-Hughes equation; circles- Kaptay equation.

4. CONCLUSION

Our theoretical investigation for the thermodynamic properties of mixing of In-Zn alloy at 700 K well explains the asymmetry observed in the properties and reveals that homo-coordination of atoms is preferred over hetero-coordination in the liquid alloy. The two sets of surface tension values obtained from the two approaches are found in excellent agreement while there is only satisfactory agreement between the two sets of results for the viscosity. Both surface tension and viscosity are found to increase with the addition of Zn atoms showing marked deviation from ideality.
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