Assessment of Surface Tension and Viscosity of In-Zn melt

R. P. Koirala[1, 2*], S.K. Yadav[2, 3, 4], B. P. Singh[1], I. S. Jha[2], D. Adhikari[2]

[1]University Department of Physics, T.M. Bhagalpur University, Bhagalpur, Bihar, India

[2]Department of Physics, M.M.A.M. Campus, Tribhuvan University, Biratnagar, Nepal

[3]Central Department of Physics, Tribhuvan University, Kirtipur, Nepal

[4]PUSET, Purwanchal University, Biratnagar, Nepal

*Corresponding author: E-mail: rpphysics@gmail.com

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, $S_{CC}(0)$ 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 $S_{cc}(0)$ are found to be greater than the ideal $S_{cc}(0)$ 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

$$G_M = RT [c_A \ln\varphi + c_B \ln(1-\varphi)] + c_A(1-\varphi)W \tag{1}$$

with

$$\phi = c_A (c_A + n c_B) \tag{2}$$

Here, R is molar gas constant; T is the temperature; W is ordering energy parameter and $n = j/i$ is the ratio of self-associates formed by like atom pairs.

(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

$$S_M = -R [c_A \ln\varphi + c_B \ln(1-\varphi)] - c_A(1-\varphi)\frac{\partial W}{\partial T} \tag{3}$$

(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

$$H_M = G_M + T S_M$$

or

$$H_M = c_A(1-\phi)[W - T\frac{\partial W}{\partial T}] \tag{4}$$

2.2. Surface Properties

(i) The first approach [7, 8] links surface tension of a binary liquid alloy, s to its bulk thermodynamic properties through the surface tension s_A and s_B, and activity coefficients γ_A and γ_B of the components A and B of the alloy, which can be expressed as:

$$\sigma = \sigma_A + Y \ln\frac{c_A^s}{\gamma_A c_A} + [p(c_B^s)^2 + q(c_B)^2]\frac{W}{\alpha} \tag{5a}$$

$$\sigma = \sigma_B + Y \ln\frac{c_B^s}{\gamma_B c_B} + [p(c_A^s)^2 + q(c_A)^2]\frac{W}{\alpha} \tag{5b}$$

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. α is the mean atomic surface area of the alloy which is calculated as:

$$\alpha = \sum c_k \alpha_k ; \qquad k = A, B \tag{6}$$

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

$$\alpha_k = 1.102 (V_k / N_A)^{2/3} \tag{7}$$

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:

$$\sigma = \sigma_A + (k_B T / \alpha)[\ln c_A^s / c_A) + p\{\ln(c_A \phi^s / c_A^s \phi)$$

$$+ (c_A^s \phi - c_A \phi^s)/c_A c_A^s\} + q\{\ln(c_A / \phi) + (\phi - c_A)/c_A\}$$

$$+ i\omega / k_B T\{p(1-\varphi^s)^2 + (q-1)(1-\varphi)^2\}] \tag{8a}$$

$$\sigma = \sigma_B + (k_B T/\alpha)[\ln c_B^s / c_B) + p\{\ln(c_B(1-\phi^s)/c_B^s(1-\phi)$$
$$+(i-j)(\varphi^s - \varphi)/i\} - q\{\ln((1-\phi)/c_B) + \phi(i-j)/i\}$$
$$+ j\omega/k_B T\{p(\phi^s)^2 + (q-1)\phi^2\} \qquad (8b)$$

with $\phi = \dot{c}_A(\dot{c}_A + \dot{y}_B)$ and $\phi^s = \dot{c}_A^s(\dot{c}_A^s + \dot{y}_B^s)$ (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]:

$$\eta = (c_A \eta_A + c_B \eta_B)(1 - 2c_A c_B . H_M / RT) \qquad (10)$$

where η and η_k represent respectively the viscosity of the alloy and of pure metal k (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, η_k with temperature T may be expressed as [13]:

$$\eta_k = \eta_{ok} \exp(E/RT) \qquad (11)$$

where, η_{k} 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:

$$\eta = \frac{h N_A}{c_A V_A + c_B V_B + V^E} \exp\left(\frac{c_A G_A^* + c_2 G_B^* - \alpha . H_M}{RT}\right) \qquad (12)$$

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

$$G_k^* = RT \ln\left(\frac{\eta_k V_k}{h N_A}\right) \qquad (k = A, B) \qquad (13)$$

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.
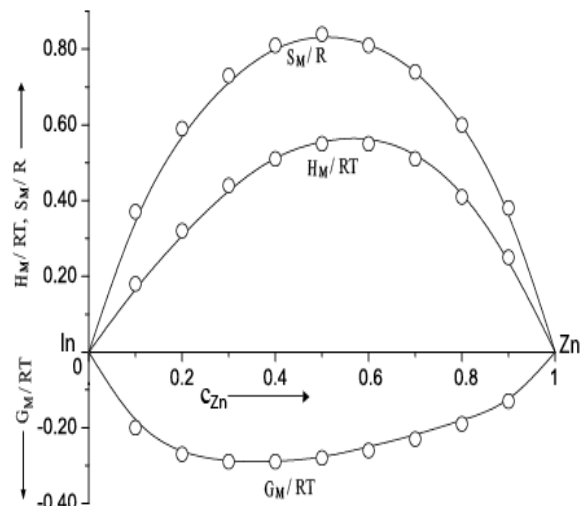

Figure 1- Free energy of mixing (G_M), entropy of mixing (S_M) and enthalpy of mixing (H_M) of In-Zn alloy at 700K versus concentration of Zn: solid curve-theory; circles-experimental [2]. Theoretically computed results for GM, SM and HM are compared with the corresponding experimental results [2]

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.
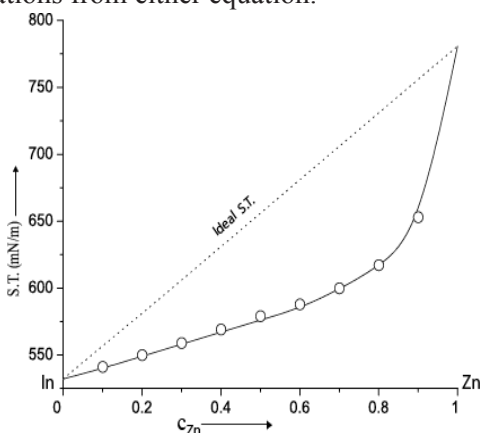

Figure 2- Surface tension of In-Zn alloy at 700K versus concentration of Zn: solid curve-layered structure approach; circles-self-associating mixture method.

The surface tension isotherm has been depicted in Figure (2). The plot shows that there is good agreement in the two sets of the results having noticeable deviations from the ideal values. The surface tension isotherm shows that the surface tension of the alloy increases with increase in concentration of Zn atoms slowly and almost linearly up to the composition $In_{0.4}Zn_{0.6}$. Above that composition, i.e. towards the Zn-rich end of the composition, a rapid increase in surface tension is noticed.

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.
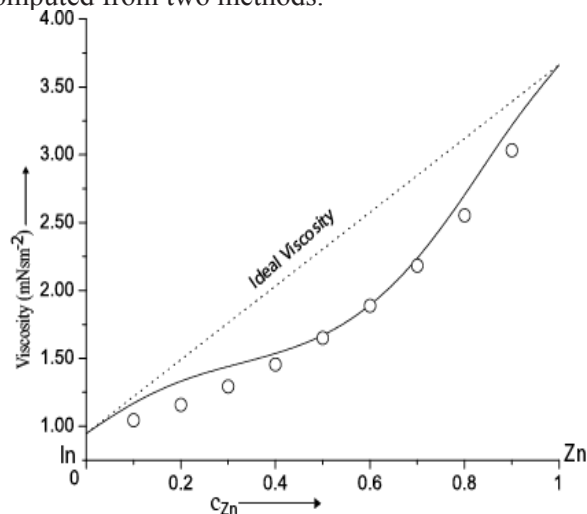

Figure 3- Viscosity of In-Zn alloy at 700K versus concentration of Zn: solid curve- Moelwyn-Hughes equation; circles- Kaptay equation.

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.

REFERENCES

[1] J. Dutkiewicz and W. Zakulski, *Bulletin of Alloy Phase Diagrams*, **5**, 284 (1984)

[2] R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser and K.K. Kelly, *Selected values of the thermodynamic properties of binary alloys*, ASM, Metal Park, OH (**1973**)

[3] C. L. Wilson and E. A. Peretti, Ind. Eng. Chem., **28**, 204 (1936)

[4] R. N. Singh and F. Sommer, Rep. Prog. Phys. **60**, 57 (1997)

[5] B. C. Anusionwu, C. A. Madu and C. E. Orji, PRAMANA- J. Physics, **72**, 951 (2009)

[6] R. P. Koirala, J. Kumar, B. P. Singh and D. Adhikari, J. Non-Cryst. Solids **394-395,** 9 (2014)

[7] B. C. Anusionwu and G. A. Adebayo, The Abdus Salam International Centre for Theoretical Physics, IC/2008/065.

[8] L. C. Prasad, R. N. Singh and G. P. Singh, Phys. Chem. Liq. **27**, 179 (1994)

[9] R. Novakovic, D. Giuranno, E. Ricci, S. Delsante, D. Li and G. Borzone, Surf. Sci. **605,** 248 (2011)

[10] I. Koirala, B. P. Singh and I. S. Jha, The Himalayan Physics, **4**, 40 (2013)

[11] L. C. Prasad and R. K. Jha, phys. stat. sol. (a) **202**, 2709 (2005)

[12] I. Budai, M. Z. Benko, G. Kaptay, Materials Science Forum, **537-538**, 489 (2007)

[13] E. A. Brandes and G. B. Brook, Smithells Metals Reference Book, **Seventh edition** 14-7, (1992)