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Research Article

THERMODYNAMIC MODELING AND ACTIVITY ANALYSIS OF Bi-In-Sn TERNARY LIQUID ALLOYS AT HIGH TEMPERATURES

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ABSTRACT

The activities of each component metal, i.e., Bi, In, and Sn in Bi-In-Sn at 1000 K, were calculated for ternary liquid alloys, which are lead-free, applying the molecular interaction volume model (MIVM). The predicted values of the activity of the component Bi and the associated experimental data were analyzed for Bi-In-Sn at 1000 K. Between the theory and experiment, there was a significant amount of agreement. Both negative and positive deviations of Bi activity, the negative activity deviation of In, and the positive activity deviation of Sn from ideal Raoult's law have been observed in Bi-In-Sn liquid alloys at 1000 K. In addition, the partial molar Gibbs free energy ($\Delta\overline{G_{Bi}}$) of Bi in Bi-In-Sn alloys at 1025 K was also calculated and compared with the available experimental data, which also shows a reasonable agreement.

Keywords: Activity, molecular interaction volume model, partial molar Gibbs free energy, solder liquid alloys, ternary alloys

INTRODUCTION

Although lead-based techniques are popular for soldering applications because of their affordability, it's important to note that lead is a hazardous metal that can lead to health and environmental issues (Abtew & Selvaduray, 2000; Knott & Mikula, 2002; Liu et al., 2004; Moelans et al., 2003). Currently, lead usage is prohibited worldwide. This prohibition is mainly due to the harmful impact on human health caused by the disposal of electronic devices such as computers, mobile phones, TV sets, and others that contain lead in their soldering processes, contaminating underground water (Ervina et al., 2008). Replacing lead in soldering mechanisms has proven to be a more cost-effective approach than draining electronic waste. This has made the development of solder free of lead a significant topic in the electronic industry. The advanced alloys should have similar properties to lead, including a melting point, non-toxicity, properties of wetting, low cost, resistance to corrosion, etc. Consequently, numerous research efforts have been undertaken to displace lead in soldering systems (Knott & Mikula, 2002).

Tin (Sn) is a delicate, silvery-white metal that gives objects luster. Its melting point is lower (505 K). Tin-based alloys are corrosion-resistant (Sah et al., 2022). Indium (In) has the ability to conduct electricity, adhere well to glass, and remain transparent. One of the main properties of bismuth (Bi) alloys is that when they solidify, they expand slightly. For this reason, bismuth has also been used in solder. This solder gives good wetting and solder flow. Furthermore, bismuth alloys have low melting points, and they are mostly used for fire detection and suppressing system safety devices. Bi-In-Sn is suitable for lead-free solder due to its low melting point, stable mechanical and microstructural properties, oxidation resistance, and compliance with environmental standards (Sah, Jha, et al., 2023; Sah, Koirala, et al., 2023).

We have chosen temperatures like 1000K and 1025K to study the Bi-In-Sn alloy system for several reasons. These temperatures often correspond to important phase transitions, providing insights into the material's stability and behavior. Under these conditions, thermodynamic and kinetic properties become key areas of study. These temperatures are also relevant for practical applications, like soldering, making the findings useful for industry. Additionally, selecting these values aligns with previous research or standards, allowing for direct comparisons and continuity in the field. At such high temperatures, Bi-In-Sn alloys are used in solders for electronics and aerospace and in nuclear reactors. They also support metallurgical processes like casting and brazing and are utilised in thermoelectric devices for converting waste heat into electricity.

Some Sn-based multicomponent alloy systems, including Sn-Cu, Al-Sn-Zn, Sn-Ag-Cu-Zn, Sn-Ag-Cu-Sb, and others, have proven to be superior alternatives to traditional Sn-Pb alloys (Abtew & Selvaduray, 2000; Amore et al., 2008; Knott & Mikula, 2002; Lee et al., 2004). Manasijevic et al. have studied the microstructure as well as the thermal characteristics of Bi-In-Sn alloys with a low melting point (Manasijević et al., 2018). The thermodynamic inquiry of Bi-In at 900 K has been performed by Yadav et al. using the regular associated solution model (Yadav et al., 2015). Asryan and Mikula investigated the thermodynamic characteristics of the Bi-Sn system between 673 and 793 K using emf of liquid

electrolyte (Asryan, N.A., & Mikula, 2004). Two distinct experimental techniques, namely torsion-effusion and differential scanning calorimetry, were utilized to examine the thermodynamic properties of Bi-In-Sn solder alloys by Brunetti et al. (Brunetti et al., 2006). The activity of indium in liquid Bi-In-Sn alloys in the temperature range of 723 K to 855 K has been measured electrochemically by Kumar et al. along three ternary sections using a molten salt electrolyte galvanic cell (Kumar et al., 2016). The activity of indium in liquid In-Bi-Sn alloys and their integral excess Gibbs free energy of mixing at 813 K have been measured by Sah et al. using MIVM (Sah, Jha, et al., 2023). The MIVM effectively predicts activities in various ternary and quaternary lead-free solder systems, showing good agreement with experimental data, making it a reliable tool for phase diagram calculations and interfacial reaction analysis (Tao, 2008). But the theoretical studies of the activities of each component, i.e., Bi, In, and Sn, along with the partial molar free energies of Bi in Bi-In-Sn liquid alloys, are lacking in the literature. Therefore, in this study, we have utilized the molecular interaction volume model (MIVM) to calculate the Bi, In, and Sn activities in the Bi-In-Sn ternary liquid alloys at 1000 K with detailed analysis. In addition, we have also calculated the partial molar free energies of Bi in Bi-In-Sn liquid alloys at 1025 K.

MATERIALS AND METHODS

The MIVM model states that liquid molecules are not like solid molecules, which oscillate constantly at one location but migrate non-randomly across molecular cells, or gas molecules, which are in constant irregular motion. The cells are moveable and identical, and the central molecules can be exchanged for their closest molecules (Tao, 2000). The activity coefficients of the components *i* and *j* in a binary liquid alloy are represented by $\boldsymbol{\gamma_i}$ and $\boldsymbol{\gamma_j}$respectively, and given (Tao, 2001) as:

$$ln\,\gamma_i = ln\left(\frac{V_{mi}}{x_iV_{mi}+x_jV_{mj}A_{ji}}\right) + x_j\left(\frac{V_{mj}A_{ji}}{x_iV_{mi}+x_jV_{mj}A_{ji}} - \frac{V_{mi}A_{ij}}{x_jV_{mj}+x_iV_{mi}A_{ij}}\right) - \frac{x_j^2}{2}\left[\frac{Z_iA_{ji}^2\,ln\,A_{ji}}{(x_i+x_jA_{ji})^2} + \frac{Z_jA_{ij}\,ln\,A_{ij}}{(x_j+x_iA_{ij})^2}\right] \quad (1)$$

$$ln\,\gamma_j = ln\left(\frac{V_{mj}}{x_jV_{mj}+x_iV_{mi}A_{ij}}\right) - x_i\left(\frac{V_{mj}A_{ji}}{x_iV_{mi}+x_jV_{mj}A_{ji}} - \frac{V_{mi}A_{ij}}{x_jV_{mj}+x_iV_{mi}A_{ij}}\right) - \frac{x_i^2}{2}\left[\frac{Z_jA_{ij}^2\,ln\,A_{ij}}{(x_j+x_iA_{ij})^2} + \frac{Z_iA_{ji}\,ln\,A_{ji}}{(x_i+x_jA_{ji})^2}\right] \quad (2)$$

In this context, V_{mi} and V_{mj} represent the molar volumes, while x_i and x_j denote the molar fractions of components *i* and *j* in a binary liquid alloy, respectively. The pair potential energy interaction parameters in binary liquid alloys are represented by A_{ij} and A_{ji}. Z_i and Z_j represent the first coordination numbers for the i^{th} and j^{th} component metals in a binary liquid alloy. The formulation for first coordination number Z_i is provided in reference (Tao, 2005) as:

$$Z_i = \frac{4\sqrt{2\pi}}{3}\left(\frac{r_{mi}^3-r_{0i}^3}{r_{mi}-r_{0i}}\right)\rho_i r_{mi}\,exp\left(\frac{\Delta H_{mi}(T_{mi}-T)}{Z_cRTT_{mi}}\right) \quad (3)$$

The molecular number density, $\rho_i = \frac{N_i}{V_{mi}}$, where N_i = 0.6022, represents the molecular number. ΔH_{mi} represents the melting enthalpy, and T_{mi} represents the melting temperature. Z_c = 12 for certain liquid metals, which corresponds to the close-packed coordination number. r_{mi} represents the first peak value of the radial distribution function, while r_{0i} signifies the initial value of the radial distribution function. The relationship between the initial value of the radial distribution function (r_{0i}) and the atomic covalent diameter ($d_{cov\,i}$) can be expressed as follows (Tao, 2008):

$$r_{0i} = 0.918d_{cov\,i} \quad (4)$$

Again, the relationship between the first peak value of the radial distribution function (r_{mi}) and atomic diameter (σ_i) can be expressed as follows (Tao, 2008):

$$r_{mi} = \sigma_i \quad (5)$$

The pair potential energy interaction parameters A_{ij} and A_{ji} are given as (Odusote et al., 2017):

$$A_{ji} = exp\left(-\frac{\varepsilon_{ji}-\varepsilon_{ii}}{KT}\right);\; A_{ij} = exp\left(-\frac{\varepsilon_{ij}-\varepsilon_{jj}}{KT}\right) \quad (6)$$

Here the pair potential energies of the pairs *i-j*, *i-i*, and *j-j* in a binary system have been denoted by ε_{ij} or ε_{ji}, ε_{ii} and ε_{jj} respectively, T refers to the absolute temperature, and K denotes the Boltzmann constant.

Now, the infinite activity coefficients; γ_i^{∞} and γ_j^{∞} for the components *i* and *j* of the binary liquid alloys are given as (Odusote et al., 2017):

$$ln\,\gamma_i^{\infty} = 1 - ln\left(\frac{V_{mj}A_{ji}}{V_{mi}}\right) - \frac{V_{mi}A_{ij}}{V_{mj}} - \frac{1}{2}\left(Z_i\,ln\,A_{ji} + Z_jA_{ij}\,ln\,A_{ij}\right) \quad (7)$$

and

$$ln\,\gamma_j^{\infty} = 1 - ln\left(\frac{V_{mi}A_{ij}}{V_{mj}}\right) - \frac{V_{mj}A_{ji}}{V_{mi}} - \frac{1}{2}\left(Z_j\,ln\,A_{ij} + Z_iA_{ji}\,ln\,A_{ji}\right) \quad (8)$$

To determine the values of A_{ij} and A_{ji}, equations (7) and (8) can be solved using the Newton-Raphson method, which provides initial values for A_{ij} and A_{ji}. During the estimation of component activities for liquid binary alloys using equations (1) and (2), the values of A_{ij} and A_{ji} are further modified slightly. Once the appropriate values of A_{ij} and A_{ji} are determined for a particular temperature, their values for other temperatures can also be obtained accordingly (Odusote et al., 2017).

For example, for the binary system Bi-In at 1000 K,

$$-\frac{\varepsilon_{ji} - \varepsilon_{ii}}{K} = T\,ln\,A_{ji} = 900\,ln\,(0.7125) = -305.0778$$

$$A_{ji} = exp\left(\frac{-305.0778}{1000}\right) = 0.7370$$

And

$$-\frac{\varepsilon_{ij} - \varepsilon_{jj}}{K} = T\,ln\,A_{ij} = 900\,ln\,(1.4322) = 323.2905$$

$$A_{ij} = exp\left(\frac{323.2905}{1000}\right) = 1.3816$$

By considering the Bi-In-Sn ternary liquid alloy as the 1-2-3 system, we can derive the formula for the activity coefficient (γ_1) of the first component of the system as (Tao, 2000):

$$ln\,\gamma_1 = 1 + ln\left(\frac{V_{m1}}{x_1V_{m1} + x_2V_{m2}A_{21} + x_3V_{m3}A_{31}}\right) - \frac{x_1V_{m1}}{x_1V_{m1} + x_2V_{m2}A_{21} + x_3V_{m3}A_{31}} - \frac{x_2V_{m1}A_{12}}{x_1V_{m1}A_{12} + x_2V_{m2} + x_3V_{m3}A_{32}} - \frac{x_3V_{m1}A_{13}}{x_1V_{m1}A_{13} + x_2V_{m2}A_{23} + x_3V_{m3}}$$
$$-\frac{1}{2}\left(\frac{Z_1(x_2A_{21}+x_3A_{31})(x_2A_{21}\,ln\,A_{21}+x_3A_{31}\,ln\,A_{31})}{(x_1+x_2A_{21}+x_3A_{31})^2} + \frac{Z_2x_2A_{12}[(x_2+x_3A_{32})\,ln\,A_{12}-x_3A_{32}\,ln\,A_{32}]}{(x_1A_{12}+x_2+x_3A_{32})^2} + \frac{Z_3x_3A_{13}[(x_2A_{23}+x_3)\,ln\,A_{13}-x_2A_{23}\,ln\,A_{23}]}{(x_1A_{13}+x_2A_{23}+x_3)^2}\right) \quad (9)$$

where x_1, x_2, and x_3 denote the molar fractions of components 1, 2, and 3 in a ternary liquid alloy, respectively.

The partial molar free energies of Bi in Bi-In-Sn liquid alloys can be given by a relation as (Knott et al., 2010):

$$\Delta\overline{G_{Bi}} = RT\,ln\,a_{Bi} = -nEF \quad (10)$$

where R is the gas constant, a_{Bi} is the activity of bismuth, T is the absolute temperature, and F is the Faraday constant, n is the number of exchanged electrons, and E is the electromotive force of the galvanic cell.

RESULTS AND DISCUSSION

Table 1 presents the required input parameters, while Table 2 displays the values of A_{ij} and A_{ji} for the binary alloys and Z_i and Z_j for the constituent elements of the binary systems. The first coordination numbers have been determined using equation (3). Equation (9) has been used to determine the activities of the Bi component in the Bi-In-Sn system at 1000 K and 1025 K. These calculated values have then been presented in Tables 3 and 6, respectively.

Table 1. Values of some input parameters (Iida & Guthrie, 1993)

Metal, i	ΔH_{mi} [kJ/mol]	r_{mi} [x10^{-8}cm]	r_{0i} [x10^{-8}cm]	V_{mi} [cm^3/mol]
Bi	11.30	3.34	2.78	20.80[1+1.17x10^{-4}(T-544)]
In	3.26	3.14	2.70	16.30[1+0.97x10^{-4}(T-430)]
Sn	7.07	3.14	2.68	17.00[1+0.87x10^{-4}(T-505)]

Table 2. Estimated A_{ji}, A_{ij}, Z_i, and Z_j values for various binary alloys at various temperatures

i-j	T[K]	A_{ji}	A_{ij}	Z_i	Z_j
Bi-In	1025	0.7425	1.3707	7.8161	8.9853
Bi-Sn	1025	0.8490	1.1065	7.8161	8.4298
In-Sn	1025	0.5037	1.4816	8.9853	8.4298
Bi-In	1000	0.7370	1.3816	7.8594	9.0131
Bi-Sn	1000	0.8456	1.1094	7.8594	8.4619
In-Sn	1000	0.4952	1.4963	9.0131	8.4619

Table 3. Values of the activity of Bi in Bi-In-Sn liquid ternary alloys at 1000 K, as determined by theory and experiment (Brunetti et al., 2006)

$\rho = {}^{x_{In}}/_{x_{Sn}} = 0.85$			a_{Bi}Th.	a_{Bi}Exp.*	Deviation from ideal Raoult's line
x_{Bi}	x_{In}	x_{Sn}			
0.000	-------	-------	0.000	-------	0.000
0.350	0.299	0.350	0.291	0.300	-0.059
0.450	0.253	0.297	0.415	0.410	-0.035
0.526	0.223	0.261	0.500	0.500	-0.026
0.589	0.189	0.222	0.578	0.590	-0.011
0.688	0.144	0.168	0.687	0.710	-0.001
0.750	0.115	0.135	0.752	0.820	0.002
0.816	0.085	0.099	0.818	0.900	0.002
0.898	0.047	0.055	0.899	0.960	0.001
1.000	-------	-------	1.000	-------	0.000

* Experimental (Brunetti et al., 2006)

From Table 3, the results show that the predicted and experimental Bi activities exhibit reasonable agreement with each other, although some discrepancies have been observed. The maximum errors, reaching up to 9.11%, have been found at a concentration of Bi, x_{Bi} = 0.816. The graphical plots of activities of Bi (a_{Bi}) vs. concentration of Bi (x_{Bi}) have been shown in Figure 1.

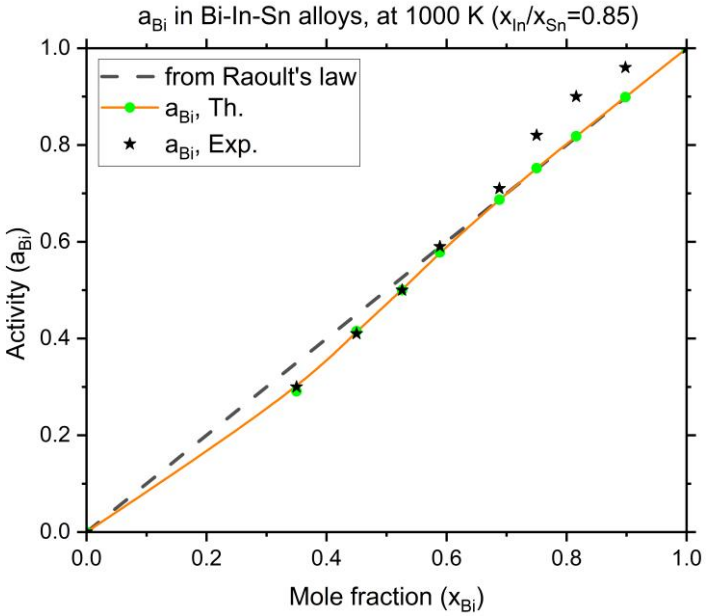

Figure 1. Theoretical and experimental comparisons of Bi activity in Bi-In-Sn liquid alloys at 1000 K with an In/Sn ratio of ρ = 0.85, showing variation with Bi concentration (Brunetti et al., 2006).

Figure 1 illustrates that the Bi activity in liquid Bi-In-Sn alloys at 1000 K in the higher concentration range of Bi, i.e., x_{Bi}, exhibits a slight discrepancy between theoretical and experimental (Brunetti et al., 2006) values. The partial vapor pressures of the component Bi in Bi-In-Sn alloys at 1000 K are lower than their equivalent vapor in the case of an ideal mixture, as demonstrated by a negative divergence from Raoult's law at the lower concentrations of x_{Bi}. This happens because the cohesive force between similar molecules (i.e., among Bi atoms) is smaller than the adhesive force between dissimilar molecules. But at higher concentrations of x_{Bi}, the theoretical Bi activity shows a small positive deviation indicating higher vapor pressure, which illustrates the ordering to segregating characteristics of the Bi-In-Sn liquid mixture at 1000 K when x_{Bi} increases. Above x_{Bi} = 0.6, the theoretical Bi activity curve becomes closer to the ideal Raoult's line, while the experimental curve shows more positive deviations. Here it is necessary to mention that as theoretical models are predicated on assumptions and simplifications, their ability to accurately depict reality may be limited. Therefore, theoretical results may not always match experimental findings since experimental results capture real-world details.

Table 4. Values of the activity of In in Bi-In-Sn liquid ternary alloys at 1000 K, as determined by theory

$\rho = {}^{x_{Sn}}/_{x_{Bi}} = 0.85$			a_{In}Th.	Deviation from ideal Raoult's line
x_{In}	x_{Sn}	x_{Bi}		
0.000	-------	-------	0.000	0.000
0.350	0.299	0.350	0.259	-0.091
0.450	0.253	0.297	0.372	-0.078
0.526	0.223	0.261	0.456	-0.070
0.589	0.189	0.222	0.539	-0.050
0.688	0.144	0.168	0.658	-0.030
0.750	0.115	0.135	0.731	-0.019
0.816	0.085	0.099	0.806	-0.010
0.898	0.047	0.055	0.895	-0.003
1.000	------	------	1.000	0.000

The activities of the component In in the system Bi-In-Sn at 1000 K with a variable concentration of In (x_{In}) all at a constant Sn/Bi ratio, i.e., (x_{Sn}/x_{Bi}) = 0.85, have been computed using Eq. (9), which has been presented in Table 4, and their graphical plots have been shown in Figure 2(a).

Table 5. Values of the activity of Sn in Bi-In-Sn liquid ternary alloys at 1000 K, as determined by theory

$\rho = {}^{x_{Bi}}/_{x_{In}} = 0.85$			a_{Sn}Th.	Deviation from ideal Raoult's line
x_{Sn}	x_{Bi}	x_{In}		
0.000	-------	-------	0.000	0.000
0.350	0.299	0.350	0.366	0.016
0.450	0.253	0.297	0.489	0.039
0.526	0.223	0.261	0.576	0.050
0.589	0.189	0.222	0.655	0.066
0.688	0.144	0.168	0.757	0.069
0.750	0.115	0.135	0.812	0.062
0.816	0.085	0.099	0.863	0.047
0.898	0.047	0.055	0.919	0.021
1.000	-------	-------	1.000	0.000

The activities of the components Sn in the system Bi-In-Sn at 1000 K with a variable concentration of Sn (x_{Sn}) all at a constant Bi/In ratio, i.e., (x_{Bi}/x_{In}) = 0.85, have been computed using Eq. (9), which has been presented in Table 5, and their graphical plots have been shown in Figure 2(b).

The activities of In deviate negatively from the ideal Raoult's line during whole concentrations of In, as seen in Figure 2(a). Initially, the negative activity deviation of In increases up to x_{In}=0.350, and then the negative activity deviation of In from the Raoult's line gradually decreases in the concentration range $0.350 \leq x_{In} \leq 1$. The interactions of the In-component with the other components in the alloy appear to be stronger than what Raoult's law would suggest, based on its negative deviation of activity. This increased attraction causes each component to be held more tightly within the mixture, resulting in lower vapor pressures than expected for ideal behavior. Here, cohesive forces are weaker than adhesive forces. As a result, the element In interacts more strongly with the alloy's other constituents than it does with itself. Because breaking adhesive connections involves more energy, this makes it energetically unfavorable for molecules of that component to escape into the vapour phase. Thus, In enhances the ordering characteristics of the Bi-In-Sn liquid mixture.

The activities of Sn deviate positively from the ideal Raoult's line during whole concentrations of Sn, as seen in Figure 2(b). The positive activity deviation of Sn from the Raoult's line gradually increases in the concentration range $0 \leq x_{Sn} \leq 0.688$, and then it decreases in the range $0.688 \leq x_{Sn} \leq 1$. The Sn component's interactions with the other components in the alloy appear to be weaker than what Raoult's law would suggest, based on its positive deviation of activity. Due to this, each component tends to escape more readily into the vapour phase, leading to higher vapor pressures than predicted by ideal behavior. Here, the cohesive forces dominate over adhesive forces. The interactions of the component Sn with itself are stronger than its interactions with other components. This makes the molecules of that component (Sn) escape into the vapor phase, leading to a higher vapor pressure. Thus, Sn enhances the segregating characteristics of the Bi-In-Sn liquid mixture.

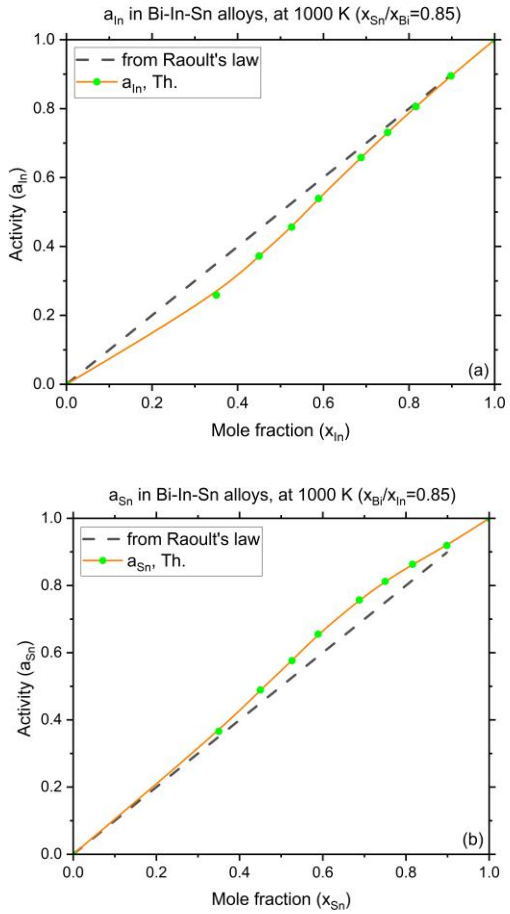

Figure 2. Theoretical analysis of (a) In activity vs. In concentration with a Sn/Bi ratio of ϱ = 0.85 and (b) Sn activity vs. Sn concentration with a Bi/In ratio of ρ = 0.85 in Bi-In-Sn liquid alloys at 1000 K.

We haven't compared our findings to those of others because there is a lack of additional theoretical or experimental studies on the activities of In and Sn in the Bi-In-Sn liquid system at 1000 K. However, we can confirm that our finding for the activity of components In and Sn in the Bi-In-Sn system should also be reasonable on the basis of valid results for the activities of component Bi in the ternary system Bi-In-Sn.

Table 6. Values of the partial molar free energies of Bi in Bi-In-Sn liquid ternary alloys at 1025 K, as determined by theory and experiment (Brunetti et al., 2006)

Different sets of compositions of alloys	x_{Bi}	x_{In}	x_{Sn}	a_{Bi}	$\Delta\overline{G_{Bi}}$Th. (kJ/mol)	$\Delta\overline{G_{Bi}}$Exp.* (kJ/mol)
A	0.197	0.803	0.000	0.114	-18.4	-18.8
B	0.200	0.700	0.100	0.116	-18.3	-17.4
C	0.196	0.604	0.200	0.113	-18.5	-18.8
D	0.200	0.400	0.400	0.123	-17.7	-15.6
E	0.200	0.100	0.700	0.171	-15.0	-16.2

* Experimental (Brunetti et al., 2006)

Table 6 illustrates that the values of the partial molar free energies of Bi in Bi-In-Sn liquid ternary alloys at 1025 K as determined theoretically agree well with the experimental data (Brunetti et al., 2006), though there are some variances, i.e., having maximum errors of 13.46% for the set D. Here it is necessary to mention that as our molar fraction data of Bi taken from literature is not varying enough, i.e., the variation of x_{Bi} is small, it is difficult to plot the graph between partial molar free energy and the mole fraction. Furthermore, we have not determined the partial molar free energies of In and Sn for Bi-In-Sn liquid ternary alloys, as there is not availability of additional theoretical and experimental data for their comparison.

CONCLUSIONS

The findings of this study demonstrate that the molecular interaction volume model provides a suitable

framework for elucidating thermodynamic phenomena such as the components' activity in a ternary system. The model successfully explains the observed negative and positive deviations of Bi activity (i.e., negative deviation at lower Bi-concentrations and small positive deviation at higher Bi-concentrations), indicating the ordering to segregating characteristics of the Bi-In-Sn liquid mixture at 1000 K when Bi-concentrations increase. The negative activity deviation of In from Raoult's law shows that its vapour pressure in the Bi-In-Sn mixture at 1000 K is lower than expected, indicating stronger attraction between In and the other components, while the positive deviation of activity of Sn from Raoult's law shows that Sn's vapour pressure in the Bi-In-Sn mixture at 1000 K is higher than expected, indicating weaker attraction between Sn and the other components. Stronger adhesive forces lower In's vapour pressure, while dominant cohesive forces raise Sn's vapour pressure in Bi-In-Sn liquid alloys at 1000 K. Furthermore, the partial molar free energies of Bi in Bi-In-Sn liquid ternary alloys at 1025 K have also been evaluated by using Bi's activities obtained from the MIV model.

AUTHORS CONTRIBUTION

S.K. Sah: Investigation, conceptualization, methodology, writing-original draft, writing-review & editing; I. Koirala: supervision, validation, conceptualization, software, review.

CONFLICT OF INTEREST

Authors declare that they don't have any known financial conflicts of interest or close personal ties that would have appeared to affect the research stated in this paper.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author, upon reasonable request.

REFERENCES

Abtew, M., & Selvaduray, G. (2000). Lead-free solders in microelectronics. *Materials Science and Engineering R: Reports*, *27*(5–6), 95–141. https://doi.org/10.1016/S0927-796X(00)00010-3.

Amore, S., Ricci, E., Lanata, T., & Novakovic, R. (2008). Surface tension and wetting behaviour of molten Cu-Sn alloys. *Journal of Alloys and Compounds*, *452*(1), 161–166. https://doi.org/10.1016/j.jallcom.2007.01.178

Asryan, N.A., & Mikula, A. (2004). Thermodynamic properties of Bi-Sn melts. *Inorganic Materials*, *40*, 386–390.

Brunetti, B., Gozzi, D., Iervolino, M., Piacente, V., Zanicchi, G., Parodi, N., & Borzone, G. (2006). Bismuth activity in lead-free solder Bi-In-Sn alloys. *Calphad*, *30*(4), 431–442. https://doi.org/10.1016/j.calphad.2006.07.003.

Ervina, E.E., Ismail, A.B., Sharif, N.M., Ariga, T., & Hussain, Z. (2008). Characteristic of low temperature of Bi-In-Sn solder alloy. *Proceedings of the IEEE/CPMT International Electronics Manufacturing Technology (IEMT) Symposium*, *33*, 1–4. https://doi.org/10.1109/IEMT.2008.5507865.

Iida, T., & Guthrie, R.I.L. (1993). *The Physical Properties of Liquid Metals*. Clarendon Press, Oxford.

Knott, S., Li, Z., Wang, C.H., & Mikula, A. (2010). Electromotive force measurements in the ternary system Bi-In-Zn. *Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science*, *41*(12), 3130–3135. https://doi.org/10.1007/s11661-010-0294-3.

Knott, S., & Mikula, A. (2002). Thermodynamic properties of liquid Al-Sn-Zn alloys: A possible new lead-free solder material. *Materials Transactions*, *43*(8), 1868–1872. https://doi.org/10.2320/matertrans.43.1868.

Kumar, M.R., Mohan, S., & Behera, C.K. (2016). Measurement of Activity of Indium in Liquid Bi-In-Sn Alloys by EMF Method. *Journal of Electronic Materials*, *45*(8), 4314–4323. https://doi.org/10.1007/s11664-016-4574-6.

Lee, J., Shimoda, W., & Tanaka, T. (2004). Surface Tension and its Temperature Coefficient of Liquid Sn-X (X = Ag , Cu) Alloys. *Materials Transactions*, *45*(9), 2864–2870.

Liu, X.J., Yamaki, T., Ohnuma, I., Kainuma, R., & Ishida, K. (2004). Thermodynamic calculations of phase equilibria, surface tension and viscosity in the In-Ag-X (X=Bi, Sb) system. *Materials Transactions*, *45*(3), 637–645. https://doi.org/10.2320/matertrans.45.637.

Manasijević, I., Balanović, L., Grgurić, T.H., Minić, D., & Gorgievski, M. (2018). Study of Microstructure and Thermal Properties of the Low Melting Bi-In-Sn Eutectic Alloys 2. Literature Review. *Materials Research*, *21*(6), 1–8.

Moelans, N., Hari Kumar, K.C., & Wollants, P. (2003). Thermodynamic optimization of the lead-free solder system Bi-In-Sn-Zn. *Journal of Alloys and Compounds*, *360*(1–2), 98–106. https://doi.org/10.1016/S0925-8388(03)00325-6.

Odusote, Y.A., Popoola, A.I., Adedayo, K.D., & Ogunjo, S.T. (2017). Thermodynamic properties of Al in ternary lead-free solder Al-Sn-Zn alloys. *Materials Science- Poland*, *35*(3), 583–593. https://doi.org/10.1515/msp-2017-0080.

Sah, S.K., Jha, I.S., & Koirala, I. (2022). Computational Study of the Thermodynamic Properties of Some Lead-free Solder Alloys. *BMC Journal of Scientific Research*, *5*(1), 69–79. https://doi.org/10.3126/bmcjsr.v5i1.50676.

Sah, S.K., Jha, I.S., & Koirala, I. (2023). Theoretical Examination of Some Thermodynamic Properties in In - Bi - Sn Liquid Alloy and its Sub - binary Systems. *Journal of Electronic Materials*, *52*(9), 6350–6359. https://doi.org/10.1007/s11664-023-10571-y.

Sah, S.K., Koirala, I., & Jha, I.S. (2023). Theoretical investigation of the thermodynamic activities of Zn-In-Sn lead-free solder alloys and the concerned binary alloys. *Materials Today: Proceedings*, https://doi.org/10.1016/j.matpr.2023.03.078.

Tao, D.P. (2000). A new model of thermodynamics of liquid mixtures and its application to liquid alloys. *Thermochimica Acta*, *363*(1–2), 105–113.

https://doi.org/10.1016/S0040-6031(00)00603-1.

Tao, D.P. (2001). Prediction of the Thermodynamic Properties of Multicomponent Liquid Alloys by Binary Infinite Dilute Activity Coefficients. In *METALLURGICAL AND MATERIALS TRANSACTIONS B* (pp. 1205–1211).

Tao, D.P. (2005). Prediction of the coordination numbers of liquid metals. *Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science*, *36*(12), 3495–3497. https://doi.org/10.1007/s11661-005-0023-5.

Tao, D.P. (2008). Prediction of activities of all components in the lead-free solder systems Bi-In-Sn and Bi-In-Sn-Zn. *Journal of Alloys and Compounds*, *457*(1–2), 124–130. https://doi.org/10.1016/j.jallcom.2007.02.123.

Yadav, S.K., Jha, L.N., & Adhikari, D. (2015). Thermodynamic and structural properties of Bi-based liquid alloys. *Physica B: Condensed Matter*, *475*, 40–47. https://doi.org/10.1016/j.physb.2015.06.015.