Journal of the Nigerian Association of Mathematical Physics
Volume 46 **(May,** ***2018 Issue*****), pp233 –242**
© J. of NAMP

THEORETICAL PREDICTION OF ALL COMPONENT ACTIVITIES IN TERNARY LEAD-FREE SOLDER ZN-IN-SN ALLOYS AT DIFFERENT TEMPERATURES

Odusote Y. A., Oluyamo S. S. and Aina O. V.

Condensed Matter Research Group, Department of Physics, The Federal University of Technology, P. M. B. 704, Akure.

Abstract

Thermodynamic activities of the constituents in the binary In-Zn,Sn- Zn and In-Sn systems have been theoretically predicted at 700 K, 750 K and 700 K, respectively, using the molecular interaction volume model (MIVM). The results obtained showed good agreement with corresponding experimental data. On this premise, we proceeded to predict the activities of all the components in ternary Zn-In-Sn alloys at the three cross-sections with a constant molar ratios of In:Sn = 1:2, 2:2, 2:1in the temperature range 753-853 K. The results obtained were compared with available experimental data. The study showed that the MIVM model could serve as an alternative approach to the time-consuming and laborious experiments in describing the activities of multicomponent alloy systems using only the corresponding binary infinite dilution activity coefficients.

1.0 Introduction

The ever increasing demands for smaller and lighter portable electronic devices in recent times have made interconnecting densities and packaging of technologies more relevant [1]. The traditional material used in electronics is Pb-Sn alloy.Pb-Sn alloy has been the major material widely used for soldering materials in electronics industry for decades due to its low cost, low melting temperature (183^{o}C), excellent strength, good electrical and wettability properties[2]. However, the presence of lead in solders is considered globally to be dangerous owning to environmental and health concerns such that small amount of lead with concentration >10µg/dl for children and >40 µg/dl for adults have been reported to be harmful to body organs like liver, kidneys and brain, thus leading to retardation and damage to nervous system [3].
In order to mitigate the health and environmental challenges caused by conventional Pb-Sn solders, efforts have been shifted to the development of new Pb-free solders for electronic interconnecting materials[1-2]. Eutectic $Au_{80}Sn_{20}$ (wt%) solders was designed and used for high-temperature applications due to its good creeping properties and high tensile strength [4]. But the main drawbacks of this kind of solders are high cost and temperature limitation in its application. On the other hand, studies have shown that Bi-based alloys can serve as substitute for conventional lead-tin solders because of their low melting point (T_m = 544.5 K at the eutectic point) and low cost [5].
It is expected that the new lead-free solder substitute being sought must meet some conditions, such as excellent electrical conductivity, suitable melting temperature as well as good substrate wettability resulting in the formation of thin intermetallic layers at the solder interface [6-7]. Other important desired properties are high strength, good resistance to mechanical and thermal fatigue, corrosion resistance; environmental friendliness and relatively less expensive material are factors to be taken into consideration in developing new solders [6-9].Both the binary and highercomponent alloy systems have been investigated either theoretically or experimentally in the search for substitute lead-free solders[3, 9-10].

Corresponding Author**:** Odusote Y.A., Email: yaodusote@futa.edu.ng, Tel: +2348052203325

Behera and Sonaye [9] measured the activity of zinc in the ternary In-Zn-Sn system in temperature range of 753-853 K using electromotive force method (EMF). The isoactivity line of zinc reflects positive deviation from the ideality at 813 K. Partial and integral enthalpies of mixing of ternary In-Sn-Zn alloy were also determined by Rechchachet al. [11]at 500^{o}C along seven sections over a large composition range using Calvet-type micro calorimeter and drop techniques. Also, vapour pressure measurement of zinc activity in In-Zn system have been performed by Yokokawa et al. [12] at 625 K using Knudsen effusion method for composition 0-30 at %zinc, while integral enthalpies of mixing of binary liquid In-Sn alloys were measured at temperature of 500^{o}C by Rechchach et al. [11].In addition, Tao et al. [13] theoretically determined the activity of components in ternary Bi-In-Sn and quaternary Bi-In-Sn-Zn lead-free solder at temperatures of 550 K and 700 K, respectively. Although, studies have indicated that Sn-based multi-component alloy systems are more favored as primary high-temperature alternatives lead-free solder [3, 10].

In this study, ternary lead-free solder Zn-In-Sn alloy and its constituent binary subsystems have been chosen as an important system in lead-free soldering for theoretical investigation. The factors that informed our choice of ternary Zn-In-Snalloys are (i) possession of low melting temperature which is one of the key characteristics of any alternative lead-free solders, and (ii) Zn-In-Sn alloy has been proposed as a promising Pb-free solder materials [9]. This study aims to complement ongoing search to find a substitute lead-free solder for common Pb-Sn solder alloys, which has become complex and widely discussed, thus prompting the industries and scientific community to look for potential lead-free solder alloys via both experiments and theoretical approaches. The predicted results of the current work will provide important in sight into both experimental and practical development of substitute lead-free solder alloys over entire range of composition of zinc in the ternary Zn-In-Sn alloys.

The molecular interaction volume model (MIVM)adopted in this study was developed by Tao [13]. The MIVM is a fluid-based model derived from statistical thermodynamics on the basis of molecular movements of liquid. It takes into account physical properties of the pure metals constituting the alloy, namely the molar volume, V_{mi} and the first coordination number, Z_i in the liquid state. These two inputs parameters are temperature dependent [14-15]. Details of the MIVM can be found in Refs. [7, 13-15, 17-18].

The paper is segmented into different sections. Section 2 gives the theoretical formulation of MIVM with results and discussion presented in section 3, and conclusion given in the last section.

2.0 Theoretical Formulation: Molecular Interaction Volume Model

According to MIVM, the molar excess Gibbs energy G_M^E of a binary liquid alloy i-j is given by [17-18]:

$$G_M^E = x_i \ln\left(\frac{V_{mi}}{x_i V_{mi} + x_j V_{mj} B_{ji}}\right) + x_j \ln\left(\frac{V_{mj}}{x_j V_{mj} + x_i V_{mi} B_{ij}}\right) - \frac{x_i x_j}{2}\left(\frac{Z_i B_{ji} \ln B_{ji}}{x_i + x_j B_{ji}} + \frac{Z_j B_{ij} \ln B_{ij}}{x_j + x_i Bi_j}\right) \tag{1}$$

where x_i *and* x_j are the molar fractions, V_{mi} *and* V_{mj} are the molar volume of component i and j, respectively. The activity coefficients of components i and j in a binary system are given as:

$$\ln\gamma_i = \ln\left(\frac{V_{mi}}{x_i V_{mi} + x_j V_{mj} B_{ji}}\right) + x_j\left(\frac{V_{mj} B_{ji}}{x_i V_{mi} + x_j V_{mj} B_{ji}} - \frac{V_{mi} B_{ij}}{x_j Vm_j + x_i V_{mi} B_{ij}}\right) - \frac{x_j^2}{2}\left[\frac{Z_i B_{ji}^2 \ln B_{ji}}{(x_i + x_j B_{ji})^2} + \frac{Z_j B_{ij} \ln B_{ij}}{(x_j + x_i B_{ij})^2}\right] \tag{2}$$

$$\ln\gamma_j = \ln\left(\frac{V_{mj}}{x_j V_{mj} + x_i V_{mi} B_{ij}}\right) + x_i\left(\frac{V_{mj} B_{ji}}{x_i V_{mi} + x_j V_{mj} B_{ji}} - \frac{V_{mi} B_{ij}}{x_j V_{mj} + x_i V_{mi} B_{ij}}\right) - \frac{x_i^2}{2}\left[\frac{Z_j B_{ij}^2 \ln B_{ij}}{(x_j + x_i B_{ij})^2} + \frac{Z_i B_{ji} \ln B_{ji}}{(x_i + x_j B_{ji})^2}\right] \tag{3}$$

Here Z_i and Z_j are the nearest neighbor molecules or first coordination numbers.

The generalized solution for equation (1) for higher order alloy system is expressed as:

$$\frac{G_m^E}{RT} = \sum_{i=1}^{N} x_i \ln \frac{V_{mi}}{\sum_{j=1}^{N} x_j V_{mj} B_{ji}} - \frac{1}{2}\sum_{i=1}^{N} Z_i x_i \left(\frac{\sum_{j=1}^{N} x_j B_{ji} \ln B_{ji}}{\sum_{j=1}^{N} x_j B_{ji}}\right) \tag{4}$$

The activity coefficient of any component *i* in a multicomponent alloy in the frame of MIVM is expressed as[17]:

$$\ln\gamma_i = 1 + \ln \frac{V_{mi}}{\sum_{j=1}^{N} x_j V_{mj} B_{ji}} - \sum_{j=1}^{N} \frac{x_j V_{mi} B_{ij}}{\sum_{l=1}^{N} x_l V_{ml} B_{lj}}$$

$$-\frac{1}{2}\left(\frac{Z_i \sum_{j=1}^{N} x_j B_{ji} \ln B_{ji}}{\sum_{l=1}^{N} x_l B_{li}} + \sum_{j=1}^{N} \frac{Z_j X_j B_{ij}}{\sum_{l=1}^{N} x_l B_{lj}} \times \left(\ln B_{ij} - \frac{\sum_{l=1}^{N} x_l B_{lj} \ln B_{lj}}{\sum_{l=1}^{N} x_l B_{lj}}\right)\right) \tag{5}$$

and, the activity of component i is obtained using**:**

$$a_i = x_i \cdot \gamma_i \tag{6}$$

The coordination number Z of the liquid metal i is calculatedusing the relation [7]:

$$Z_i = \frac{4\sqrt{2}\pi}{3}\left(\frac{r_{mi}^3 - r_{0i}^3}{r_{mi} - r_{0i}}\right)\rho_i r_{mi} \exp\left(\frac{\Delta H_{mi}(T_{mi} - T)}{Z_c RTT_{mi}}\right) \tag{7}$$

where ρ_i is the molecular number density, ΔH_{mi} and T_{mi} are the melting enthalpy and melting temperature, respectively. $Z_c = 12$ Is a closed-packed coordination, r_{oi} and r_{mi} are the beginning nd first peak values of radial distance in a radial distribution function near its melting point and R is the gas constant.

The pair-potential energy interaction parameters B_{ji} and B_{ij} are defined as[18]:

$$B_{ji} = \exp\left[-\frac{\varepsilon_{ji} - \varepsilon_{ii}}{kT}\right] \text{and } B_{ij} = \exp\left[-\frac{\varepsilon_{ij} - \varepsilon_{jj}}{kT}\right] \tag{8}$$

ε_{ii} and ε_{jj} are the i-i, j-j and i-j pair-potential energies with $\varepsilon_{ji} = \varepsilon_{ij}$ and k is the Boltzmann constant and T is the absolute temperature. The expression of infinite dilute activity coefficients Υ_i^∞ and Υ_j^∞ in a binary system i-j can be obtained from equation (5) when X_i or $X_j \to 0$, leading to

$$\ln \gamma_i^\infty = 1 - \ln\left(\frac{V_{mj} B_{ji}}{V_{mi}}\right) - \frac{V_{mi} B_{ij}}{V_{mj}} - \frac{1}{2}(Z_i \ln B_{ji} + Z_j B_{ij} \ln B_{ij}) \tag{9}$$

$$\ln \gamma_j^\infty = 1 - \ln\left(\frac{V_{mi} B_{ij}}{V_{mj}}\right) - \frac{V_{mj} B_{ji}}{V_{mi}} - \frac{1}{2}(Z_j \ln B_{ij} + Z_i B_{ji} \ln B_{ji}) \tag{10}$$

The values of B_{ji} and B_{ij} defined in Eqn. (8) at a given temperature can be determined by solving equations(9) and (10) simultaneously while their values at any other temperature desired for calculation can be obtained by assuming that the pair-potential energy parameters are independent of temperature.

Now, allowing the investigated Zn-In-Sn ternary alloy to be the 1–2–3 system, the activity coefficient of the component 1 of this system can be obtained from equation (5) as:

$$\begin{aligned}
\ln\gamma_1 = {} & 1 + \ln\left(\frac{V_{m1}}{x_1 V_{m1} + x_2 V_{m2} B_{21} + x_3 V_{m3} B_{31}}\right) - \frac{x_1 V_{m1}}{x_1 V_{m1} + x_2 V_{m2} B_{21} + x_3 V_{m3} B_{31}} \\
& - \frac{x_2 V_{m1} B_{12}}{x_1 V_{m1} B_{12} + x_2 V_{m2} + x_3 V_{m3} B_{32}} - \frac{x_3 V_{m1} B_{13}}{x_1 V_{m1} B_{13} + x_2 V_{m2} B_{23} + x_3 V_{m3}} \\
& - \frac{1}{2}\left(\frac{Z_1 (x_2 B_{21} + x_3 B_{31})(x_2 B_{21} \ln B_{21} + x_3 B_{31} \ln B_{31})}{(x_1 + x_2 B_{21} + x_3 B_{31})^2} + \frac{Z_2 x_2 B_{12}\left[(x_2 + x_3 B_{32}) \ln B_{12} - x_3 B_{32} \ln B_{32}\right]}{(x_1 B_{12} + x_2 + x_3 B_{32})^2}\right. \\
& \left. + \frac{Z_3 x_3 B_{13}\left[(x_2 B_{23} + x_3) \ln B_{13} - x_2 B_{23} \ln B_{23}\right]}{(x_1 B_{13} + x_2 B_{23} + x_3)^2}\right)
\end{aligned} \tag{11}$$

3.0 Results and discussion

3.1 Activities of components in the binary liquid Zn-In, In-Sn and Zn-Sn systems

With the use of the theoretical formulation presented in the previous section, the activities of components in the binary liquid Zn-In, In-Sn and Sn-Zn systems were first calculated at temperatures of 700 K, 700 K and 750 K, respectively. This was done in order to check the suitability of the MIVM in predicting thermodynamic activities of components in the binary systems and compare the calculated activities results obtained using the model with available experimental data taken from Hultgren et al. [19] for each liquid alloy investigated. The essential physical parameters of the pure metals required for the model calculations were taken from Iida and Guthrie [16]. The parameters are shown in the table 1. The coordination numbers Z_i's and Z_j's of the components of each binary alloy were calculated using equation (7). In computing the activities, the required pair-potential parameters B_{ji} and B_{ij} were calculated using equation (8) and simultaneous solution of equations (9) and (10). In table 2, the B_{ij} and B_{ji} along with the Z_i and Z_j of components of the binary systems are listed.

Table 1: Some essential parameters of the pure metalsused for the calculations [16]

Metals	ΔH_{mi}(kJ/Mol)	$\sigma_{oi}(\times 10^{-8} cm)$	$\sigma_{mi}(\times 10^{-8} cm)$	$V_{mi} = V_m[1 + \alpha(T - Tm)]$
Mg	8.80	2.52	3.10	$15.3[1+1.6\times10^{-4}(T-923)]$
In	3.26	2.70	3.14	$16.3[1+0.97\times10^{-4}(T-430)]$
Zn	7.28	2.16	2.66	$9.94[1+1.5\times10^{-4}(T-693)]$
Sn	7.07	2.68	3.14	$17.0[1+0.87\times10^{-4}(T-505)]$

Table 2: Computed values of B_{ji}, B_{ij}, Z_i and Z_j **for the constituents of the binary liquid alloys atdifferent temperatures**

i-j	T(K)	B_{ji}	B_{ij}	Z_i	Z_j
Zn-In	753	0.64554	1.04483	9.34439	9.65028
	773	0.65289	1.04364	9.31669	9.63217
	793	0.65995	1.04252	9.28916	9.61411
	813	0.66673	1.04145	9.26178	9.59613
	833	0.67325	1.04044	9.23457	9.57822
	853	0.67953	1.03947	9.20751	9.56037
In-Sn	753	0.35949	1.85301	9.65028	9.33343
	773	0.36914	1.82367	9.63217	9.31756
	793	0.37853	1.79625	9.61411	9.30175
	813	0.38769	1.77055	9.59613	9.28598
	833	0.39661	1.74643	9.57821	9.27027
	853	0.40530	1.72375	9.56037	9.25462
Zn-Sn	753	0.61349	1.13204	9.65028	9.33343
	773	0.62130	1.12841	9.63217	9.31756
	793	0.62881	1.12498	9.61411	9.30175
	813	0.63602	1.12172	9.59613	9.28598
	833	0.64297	1.11864	9.57822	9.27027
	853	0.64966	1.11569	9.56037	9.25462

The component activities of the binary liquid In-Zn, In-Sn and Sn-Zn alloys at respective temperature of 700 K, 700 K and 750 K were computed by substituting the corresponding values of B_{ji},B_{ij}, V_{mi},V_{mj}, Z_i and Z_j into the equations (2)and (3). The predicted and experimental results for the activities are presented in Fig. 1, Fig. 2 and Fig. 3 for each binary liquid alloy, respectively.The experimental data were taken from Hultgren et al. [19]. From the figures, it is clearly seen that there is a reasonably good agreement between the calculated results and the respective experimental data shown as symbols in the figures.

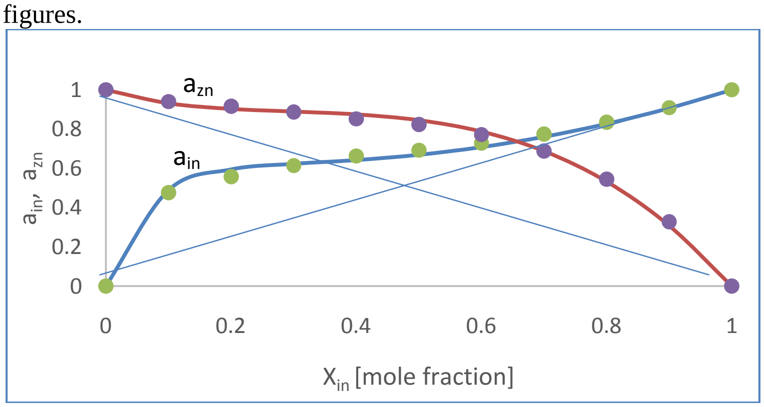


Fig. 1.Concentration dependence of a_{Zn} and a_{In} activities for liquid Zn-In alloys at 700 K.
The dotted circle and solid line denote the experimentalandtheoretical activity, respectively. (The Raoult's law).

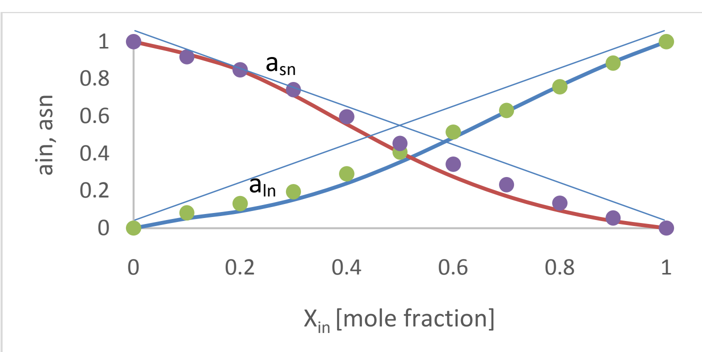


Fig. 2. Concentration dependence of a_{In} and a_{sn} activities for liquid In-Sn alloys at 700 K.

The dotted circle and solid line denote the experimental and theoretical activity, respectively. (The Raoult's law).

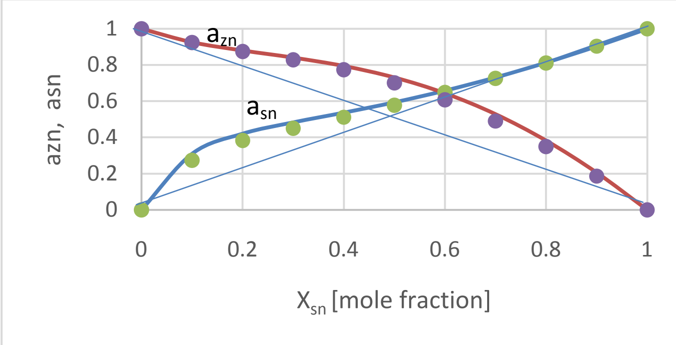
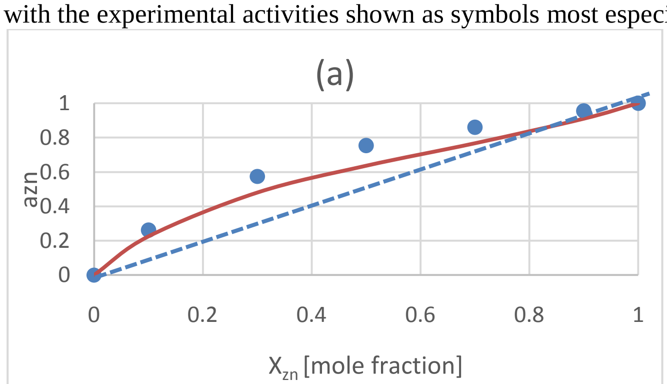


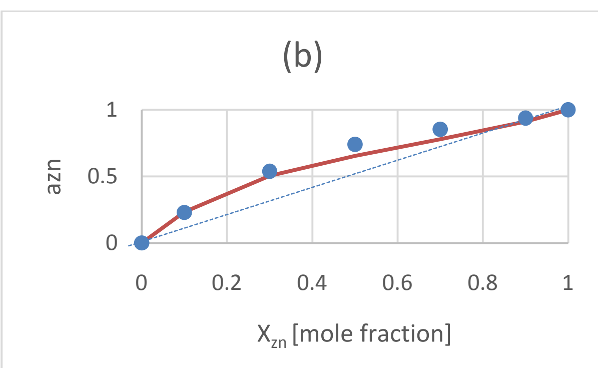
Fig. 3. Concentration dependence of a_{Zn} and a_{Sn} activities for liquid Zn-Sn alloys at 750 K
The dotted circle and solid line denote the experimental and theoretical activity, respectively (Raoult's law).

3.2 Prediction of activities of all components in ternary Zn-In-Sn system in the temperature range of 753-853 K.

On the basis of the reasonable agreement between the calculated results obtained using the MIVM and experimental results for all the binary subsystems of ternary Zn-In-Sn systems, we are assured to proceed to apply the MIVM to calculate the activity coefficients of components of the ternary Zn-In-Sn systems at different temperatures. The activity of Zn content in ternary Zn-In-Sn alloy melts were calculated by inserting the corresponding values of parameter B_{ij} and B_{ji} shown in table 2 into equation (11) and the results obtained were compared with the experimental data taken from Ref. [9] at different temperatures ranging from 753-853 K. The results of the calculated activities of Zn at the three sections with constant molar ratio of 2:1, 1:1 and 1:2 with the concentrations varying between 0 to1 at temperature of 753 K are presented in Fig. 4.

From Fig. 4 (a, b and c), it is observed that the activity of Zn exhibits positive deviation from Raoult law in the whole concentration range between 0 and 1. The positive deviation suggests tendency of clustering of atoms of In and Sn as second nearest neighbors. A more careful perusal of figures 4 reveals that the predicted activities values compared reasonably well with the experimental activities shown as symbols most especially at the cross sections with In:Sn = 1:1 and 1:2.





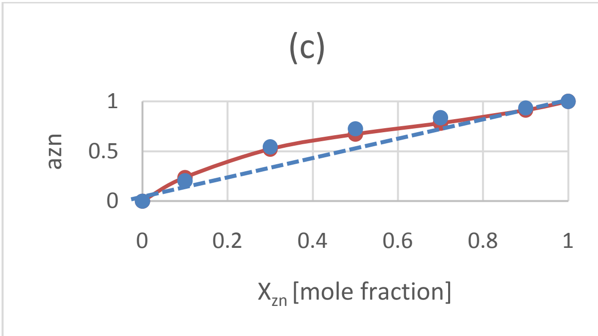


Fig. 4. Concentration dependence of Zn activity in ternary Zn-In-Sn systems calculated using Equation (11) at 753 K together with the experimental data [9]. The dottedcircles and the solid line denote the experimental and calculated activity values, respectively.Thedash line is the Raoult law. (a) ForIn:Sn= 2:1 cross-section, (b) For In:Sn = 1:1 cross-section, and (c) For In:Sn 2:1 cross-section.

The results of the calculated thermodynamic activities of components in the ternary Zn-In-Sn alloys at other temperatures 753 K, 773 K, 793 K, 813 K, 833 K and 853 K of investigation with same constant molar ratio of 2:1, 1:1 and 1:2 along with the concentrations of Zn, In and Sn are presented in tabular from in Table 3 to Table 8, respectively.

Table 3: Predicted values of component activities of Zn, In and Sn in ternary Zn-In-Sn alloys at 753 K across the three cross-sections.

In:Sn 2:1

x_{Zn}	x_{In}	x_{Sn}	a_{Zn}	a_{In}	a_{Sn}	$a_{Zn\ EXPT.[9]}$
0.1000	0.5960	0.3000	0.2328	0.4689	0.1168	0.2620
0.3000	0.4666	0.2333	0.5044	0.1745	0.2610	0.5740
0.5000	0.3333	0.1677	0.6588	0.1027	0.2652	0.7540
0.6999	0.2000	0.1000	0.7781	0.0717	0.1708	0.8600
0.9999	0.0660	0.0333	0.9117	0.0356	0.0532	0.9550

In:Sn 1:1

0.1000	0.4499	0.4499	0.2328	0.4689	0.1168	0.2290
0.3000	0.3488	0.3488	0.5044	0.1745	0.2610	0.5380
0.5000	0.2500	0.2500	0.6588	0.1027	0.2652	0.7400
0.6999	0.1500	0.1500	0.7781	0.0717	0.1708	0.8530
0.9999	0.0499	0.0499	0.9117	0.0356	0.0532	0.9380

In:Sn 1:2

0.1000	0.3000	0.5960	0.2378	0.2175	0.2569	0.2030
0.3000	0.2333	0.4666	0.5218	0.0666	0.3877	0.5450
0.5000	0.1677	0.3333	0.6705	0.0401	0.3301	0.7260
0.6999	0.1000	0.2000	0.7815	0.0306	0.2042	0.8360
0.9000	0.0333	0.0660	0.9117	0.0168	0.0671	0.9340

Table 4: Predicted values of component activities of Zn, In and Sn in ternary Zn-In-Sn alloys at 773 K across the three cross-sections.

In:Sn 2:1

x_{Zn}	x_{In}	x_{Sn}	a_{Zn}	a_{In}	a_{Sn}	$a_{Zn\ EXPT.[9]}$
0.1000	0.6000	0.2900	0.3428	0.6698	0.0642	0.2330
0.3000	0.4670	0.2333	0.5823	0.2978	0.1848	0.5370
0.5000	0.3333	0.1600	0.6874	0.1829	0.2051	0.7270
0.6999	0.2000	0.1000	0.7845	0.1251	0.1299	0.8570
0.9000	0.0667	0.0333	0.9121	0.0589	0.0375	0.9520

In:Sn 1:1

0.1000	0.4499	0.4499	0.3256	0.4670	0.1137	0.2200
0.3000	0.3488	0.3488	0.5873	0.1667	0.2476	0.5210
0.5000	0.2500	0.2500	0.6999	0.0971	0.2525	0.7270
0.6999	0.1500	0.1500	0.7921	0.0678	0.1653	0.8490
0.9999	0.0499	0.0499	0.9132	0.0337	0.0526	0.9360

In:Sn 1:2

0.1000	0.2900	0.6000	0.3036	0.2196	0.2466	0.1940
0.3000	0.2333	0.4670	0.5827	0.0647	0.3642	0.5210
0.5000	0.1600	0.3333	0.7011	0.0386	0.3108	0.7160
0.6999	0.1000	0.2000	0.7921	0.0294	0.1955	0.8270
0.9999	0.0333	0.0667	0.9129	0.0160	0.0660	0.9330

Table 5: Predicted values of component activities of Zn, In and Sn in ternary Zn-In-Sn alloys at 793 K across the three cross-sections.

In:Sn 2:1

x_{Zn}	x_{In}	x_{Sn}	a_{Zn}	a_{In}	a_{Sn}	$a_{Zn\ EXPT.[9]}$
0.1000	0.6000	0.2900	0.3302	0.6733	0.0687	0.2410
0.3000	0.4670	0.2333	0.5719	0.2987	0.1889	0.5430
0.5000	0.3333	0.1600	0.6818	0.1825	0.2064	0.7310
0.6999	0.2000	0.1000	0.7821	0.1238	0.1301	0.8450
0.9000	0.0667	0.0333	0.9117	0.0577	0.0375	0.9490

In:Sn 1:1

0.1000	0.4499	0.4499	0.3134	0.4731	0.1187	0.2150
0.3000	0.3488	0.3488	0.5758	0.1689	0.2507	0.5130
0.5000	0.2500	0.2500	0.6933	0.0978	0.2533	0.7310
0.6999	0.1500	0.1500	0.7893	0.0676	0.1654	0.8450
0.9999	0.0499	0.0499	0.9128	0.0332	0.0526	0.9320

In:Sn 1:2

0.1000	0.2900	0.6000	0.2929	0.2263	0.2509	0.1900
0.3000	0.2333	0.4670	0.5712	0.0668	0.3648	0.5190
0.5000	0.1600	0.3333	0.6942	0.0394	0.3105	0.6950
0.6999	0.1000	0.2000	0.7892	0.0296	0.1954	0.8280
0.9999	0.0333	0.0667	0.9125	0.0159	0.0660	0.9310

Table 6: Predicted values of component activities of Zn, In and Sn in ternary Zn-In-Sn alloys at 813 K across the three cross-sections.

In:Sn 2:1

x_{Zn}	x_{In}	x_{Sn}	a_{Zn}	a_{In}	a_{Sn}	$a_{Zn\ EXPT.[9]}$
0.1000	0.6000	0.2900	0.3186	0.6763	0.0725	0.2190
0.3000	0.4670	0.2333	0.5623	0.2997	0.1918	0.5240
0.5000	0.3333	0.1600	0.6765	0.1820	0.2071	0.7160
0.6999	0.2000	0.1000	0.7799	0.1226	0.1302	0.8410
0.9000	0.0667	0.0333	0.9114	0.0567	0.0375	0.9320

In:Sn 1:1

0.1000	0.4499	0.4499	0.3023	0.4784	0.1226	0.2100
0.3000	0.3488	0.3488	0.5651	0.1711	0.2527	0.5130
0.5000	0.2500	0.2500	0.6869	0.0984	0.2537	0.7130
0.6999	0.1500	0.1500	0.7866	0.0674	0.1654	0.8350
0.9000	0.0499	0.0499	0.9124	0.0328	0.0526	0.9320

In: Sn 1:2

0.1000	0.2900	0.6000	0.2833	0.2324	0.2539	0.1830
0.3000	0.2333	0.4670	0.5604	0.0689	0.3647	0.5030
0.5000	0.1600	0.3333	0.6878	0.0403	0.3099	0.6920
0.6999	0.1000	0.2000	0.7866	0.0298	0.1953	0.8210
0.9000	0.0333	0.0667	0.9122	0.0158	0.0661	0.9310

Table 7: Predicted values of component activities of Zn, In and Sn in ternary Zn-In-Sn alloys at 833 K across the three cross-sections.

In:Sn = 2:1

x_{Zn}	x_{In}	x_{Sn}	a_{Zn}	a_{In}	a_{Sn}	$a_{Zn\ EXPT.[9]}$
0.1000	0.6000	0.2900	0.3079	0.6786	0.0767	0.2250
0.3000	0.4670	0.2333	0.5532	0.3005	0.1951	0.5160
0.5000	0.3333	0.1600	0.6715	0.1816	0.2079	0.7060
0.6999	0.2000	0.1000	0.7777	0.1215	0.1302	0.7910
0.9000	0.0667	0.0333	0.9111	0.0557	0.0375	0.9210

In:Sn: 1:1

0.1000	0.4499	0.4499	0.2922	0.4829	0.1270	0.2020
0.3000	0.3488	0.3488	0.5549	0.1731	0.2552	0.4920
0.5000	0.2500	0.2500	0.6809	0.0989	0.2542	0.7030
0.6999	0.1500	0.1500	0.7839	0.0672	0.1655	0.8370
0.9000	0.0499	0.0499	0.9120	0.0323	0.0526	0.9270

In:Sn: 1:2

0.1000	0.2900	0.6000	0.2745	0.2379	0.2573	0.1790
0.3000	0.2333	0.4670	0.5504	0.0708	0.3649	0.4930
0.5000	0.1600	0.3333	0.6817	0.0410	0.3095	0.6840
0.6999	0.1000	0.2000	0.7840	0.0299	0.1952	0.8160
0.9000	0.0333	0.0667	0.9118	0.0156	0.0661	0.9290

Table 8: Predicted values of component activities of Zn, In and Sn in ternary Zn-In-Sn alloys at 853 K across the three cross-sections.

In:Sn = 2:1

x_{Zn}	x_{In}	x_{Sn}	a_{Zn}	a_{In}	a_{Sn}	$a_{Zn\ EXPT.[9]}$
0.1000	0.6000	0.2900	0.2981	0.6806	0.0809	0.2210
0.3000	0.4670	0.2333	0.5445	0.3013	0.1984	0.4980
0.5000	0.3333	0.1600	0.6666	0.1812	0.2088	0.6920
0.6999	0.2000	0.1000	0.7757	0.1203	0.1303	0.7860
0.9000	0.0667	0.0333	0.9108	0.0547	0.0375	0.9180

In-Sn : 1:1

0.1000	0.4499	0.4499	0.2828	0.4869	0.1313	0.1950
0.3000	0.3488	0.3488	0.5455	0.1749	0.2576	0.4770
0.5000	0.2500	0.2500	0.6753	0.0995	0.2547	0.6950
0.6999	0.1500	0.1500	0.7816	0.0669	0.1655	0.8370
0.9000	0.0499	0.0499	0.9117	0.0318	0.0526	0.9220

In:Sn: 1:2

0.1000	0.2900	0.6000	0.2664	0.2431	0.2607	0.1730
0.3000	0.2333	0.4670	0.5412	0.0727	0.3653	0.4840
0.5000	0.1600	0.3333	0.6759	0.0418	0.3091	0.6760
0.6999	0.1000	0.2000	0.7816	0.0302	0.1951	0.8110
0.9000	0.0333	0.0667	0.9115	0.0155	0.0661	0.9290

Tables 3 to 8 show the concentrations of the individual components of the ternary alloy, the calculated thermodynamic activities of components in this work using MIVM and the corresponding experimental activities of Zn used for validation of the calculated results across the investigated temperatures. It is evidently clear from the tables that the calculated activities of Zn compared reasonably well with the respective measured data of Zn in the ternary Zn-In-Snsystem. The predicted activities of components exhibit positive deviation with respect to Raoult's law across the molar ratio up to ≈ 93 mol% Zn, which suggests the tendency of clustering of In and Sn in the second nearest neighborhood (See Fig. 4).In addition, a proper examination of the calculated activities shows that the activity of components of the ternary Zn-In-Sn alloys decreases across the molar ratio 2:1, 1:1 and 2:1 as the temperature of the alloy increases from 753 K to 853 K. An indication that the ternary Zn-In-Sn alloys tends towards ideality with increasing temperature. Thus, the investigation of the ternary Zn-In-Sn system yields a consistent set of thermodynamic data of the liquid alloys, which are considered very important, for development of a lead-free solders database, for the design of new lead-free solders and also for the prediction of some physical and chemical properties of lead-free solders, such as surface tension and viscosity.

4.0 Conclusion

The fluid-based MIVM model of molecular movements of liquid has been used to predict the thermodynamic activities of all components in the lead-free ternary Zn-In-Sn system in the temperature range 753to 853 K along three ternary sections with constant molar ratios of 2:1, 1:1 and 2:1, respectively. The predicted activities values are in good agreement with the experimental data. The activity of Zn shows positive deviation from ideality in the entire concentration range. The activity of In also shows slightly negative deviation from ideality. The present calculations show that the MIVM is a reliable and convenient approach for predicting thermodynamic behavior of multicomponent systems due to its good physical basis.

References

[1] E.P. Wood and K.L. Nimmo, J. Electro. Mater. 23 (1994) 709-713.
[2] J. Kloeser., E. Zakel., F. Bechtold., H. Reichl, IEE COMT 19A (1996) 24-33
[3] S. Knott., C.J. Chem., F. Gehringer., A. Mikula. Inter. J. Mater. 97 (2006) 8.
[4] Z. Guo, W. Yuan, M. Hindler, A. Mikula, J. Chem. Thermodynamic 48 (2012) 201-206.
[5] Y. Takaku., I. Ohnuma., R. Kainuma., Y. Yamada., Y. Yagi., Y. Nishibe., K. Inshida, J. Electro. Mater. 35 (2006) 1926 – 1932.
[6] V. Laurila., V. Vuorinen., J.K. Kivilahti.. Mater. Sci. Eng. R, 49 (1-2) (2005). 1.
[7] Y.A. Odusote, A.I. Popoola, K.D. Adedayo and S.T. Ogunjo, Materials Science-Poland, 35(3) (2017) 583-593.
[8] Y.A. Odusote., A.I. Popoola., S.S. Oluyamo, Applied Physics A122(2) (2016) 80.
[9] C.K BeheraandA.Sonaye,ThermochimicaActa 568 (2013) 196 – 203.
[10] M. Abtew., G. Selvaduray., Mater.Sci.Eng. R.27 (2000). 95.
[11] M. Rechchach, A. Sabbar, H. Flandorfer, H. Ipser, Thermochim. Acta 502 (2010) 66-72.
[12] T. Yokokawa, A. Doi, K. Niwa, J. Phys.Chem. 65 (1961) 202-205.
[13] D.P. Tao, Thermochim.Acta 363 (2000) 105-113.
[14] D.P. Tao, Metall. Mater. Trans. A 35A (2005)3495-3497.
[15] D.P. Tao, J. Mater. Sci. Technol., 22(4) (2006) 559.

[16] T. Iida, R. I. Guthrie, The physical properties of liquid metals, Clarendon Press, Oxford, UK, 1988.

[17] D. P. Tao, J. Alloys and Compds 457 (2008) 124.

[18] D. P. Tao, J. Alloys and Compds 457 (2008) 124-130.

[19] R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Kelly, Selected values of the Thermodynamic properties of binary alloys, American Society for Metals, Metals Park, Ohio, 1973.