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Thermodynamic and Structural Estimation of Bi-Tl at 750 K

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Abstract

The thermodynamic functions like excess free energy of mixing, free energy of mixing, activity, entropy of mixing, enthalpy of mixing and thermodynamic function such as concentration, fluctuations short-order parameter as well as thermodynamic Aproperties namely diffusivity ratio of Bi-Tl melts at 750 K are investigated as function of concentration in the framework of the quasi-lattice model which is a complex formation model. The theoretical results for thermodynamic functions and microscopic functions like concentration fluctuations are in well agreement with correlated experimental data. The results reveal that Bi-Tl melt at 750 K exhibits non-ideal behaviour with a strong tendency towards chemical ordering and there is a tendency of complex formation. Again, the agreement between the theoretical results and experimental results demonstrates the reliability of the quasi-lattice model for describing the mixing behaviour of Bi-Tl melt.

Keywords

Thermodynamic Properties, Short-Range Order, Chemical Ordering, Quasi-Lattice Model

1. Introduction

Experimental measurements remain a fundamental approach for determining the thermodynamic behaviour of binary and multicomponent metallic systems. However, direct experimental characterization over broad composition and temperature ranges is often limited by high cost, significant time requirements, and practical difficulties in accessing complete datasets [1] [2]. As a result, theoretical

modelling has become an essential complement to experiments for forecasting thermodynamic properties of the systems.

Bismuth (Bi) is a low-melting, environmentally safer metal that finds utility in fusible alloys, soldering applications, and safety devices due to its unique combination of expansion upon solidification, good wetting characteristics, and corrosion resistance [3]-[5]. In contrast, thallium (TI) is a relatively soft and dense metal with a low melting point and good electrical conductivity, giving it specialized applications in electronic materials and functional alloys [6] [7]. The Bi-T1 binary alloy system has garnered interest because of its low melting behaviour, potential use in low-temperature solders, thermoelectric applications, and safety components [8] [9].

A comprehensive understanding of the thermodynamic behaviour of Bi-Tl alloys is crucial for optimizing their performance in technological applications. Although several experimental studies have been conducted on various Bi-based binary systems, reliable thermodynamic data for the Bi-TI system-particularly at elevated temperatures such as 750 K still limited [10]-[12]. This lack of data highlights the need for predictive theoretical approaches that can extend and supplement empirical findings. In the past thermodynamic and structural properties of Bi-Tl alloy at 750 K have been analysed by regular associated solution model [13].

To bridge this gap, a variety of thermodynamic models have been developed. These include geometric approaches such as the Kohler, Muggianu, and Chou models, as well as statistical thermodynamic Formalisms [14]-[16]. Among these, the quasi-lattice model, which is a complex formation model, has emerged as a robust and versatile framework for describing liquid alloys that display significant short-range ordering and strong heteroatomic interactions. The model incorporates an assumption of chemical complex formation in the liquid state and explicitly accounts for nearest-neighbour atomic interactions, offering a more realistic representation of non-ideal solution behaviour than simpler models [17] [18]. The phase diagram [1] indicates the existence of Bi-Tl and Bi_3Tl_2 complexes in the solid state of Bi-Tl alloys. In present case, it is assumed that Bi_3Tl_2 complex also exists in Bi-Tl molten alloys at 750 K.

The quasi-lattice model has been successfully applied to a range of binary alloy systems to predict key thermodynamic functions, including component activities, excess Gibbs free energy of mixing, and enthalpy of mixing, with good agreement to experimental trends where available [19]-[21]. Its relative simplicity and capacity to incorporate interaction parameters make it especially useful for systems such as Bi-Tl, where non-ideal effects are expected to be significant.

In the present study, the quasi-lattice model is employed to examine the thermodynamic properties of the liquid Bi-Ti alloys. The activities of Bi and TI, the excess Gibbs free energy of mixing, G_M^{XS}, free energy of mixing, G_M, enthalpy of mixing, H_M, entropy of mixing, S_M, concentration fluctuation, $S_{cc}(0)$, short-range order parameter, α_1, as well as diffusivity ratio, $\frac{D_M}{D_{id}}$ are calculated in order to gain insight into strength of atomic interactions, ordering tendencies, and overall

stability of the alloy. These theoretical results are anticipated to enhance the understanding of the Bi-Tl system and support its technological applications.

2. Formalism

2.1. Thermodynamic Properties i.e. G_M^{XS}, G_M, Activity, H_M, S_M of the Binary Melts

The quasi-lattice model [17] [19] [22] is a statistical mechanical model based on the grand partition function. In this model, it is considered that a given nearest neighbour bond has different energy if it belongs to the complex and if it does not. The basic concept of the quasi-lattice model is that a compound forming A-B alloy can be regarded as a pseudo ternary mixture containing A-atoms, B-atoms and complexes $A_\mu B_\nu$ with μ and ν as small integers. Such an alloy in solid state forms the chemical compounds or chemical complexes like $A_\mu B_\nu$ at one or more well specified compositions known as stoichiometric compositions, specified by $C_c = \frac{\mu}{\mu+\nu}$. The complexes *i.e.* the privileged group of atoms are considered to be existed in the molten state [11] having just μA atoms of element A and νB atoms of element B such that $\mu A + \nu B \rightleftharpoons A_\mu B_\nu$.

The free energy of mixing, G_M of a molten binary system is given by [17]

$$G_M = G_M^{XS} + G_M^{id}$$

with,

$$G_M^{id} = Nk_BT\left[c\ln c + (1-c)\ln(1-c)\right]$$

Hence,

$$G_M = G_M^{XS} + Nk_BT\left[c\ln c + (1-c)\ln(1-c)\right] \tag{1}$$

where, N represents the total number of atoms of A and B in the system, c is the composition of atom A and (1-c) is the composition of atom B, T is the absolute temperature and k_B is Boltzmann constant. It is to be mentioned that the phase diagram [1] indicates the existence of Bi-Tl complex in Bi-Tl alloys at 750 K. Thus, while deriving the equations for the different thermodynamic functions, the values of μ and ν are taken to be 3 and 2 respectively. Now the accurate equation for G_M^{XS} for $\mu = 3$ and $\nu = 2$ is expressed as [17]

$$\frac{G_M^{XS}}{RT} = \frac{\omega}{k_BT}\phi(c) + \frac{\Delta\omega_{AB}}{k_BT}\phi_{AB}(c) + \frac{\Delta\omega_{AA}}{k_BT}\phi_{AA}(c) + \frac{\Delta\omega_{BB}}{k_BT}\phi_{BB}(c) \tag{2}$$

where,

$$\phi(c) = c(1-c) \tag{3a}$$

$$\phi_{AB}(c) = \frac{13}{420}c + \frac{2}{3}c^3 - \frac{3}{2}c^4 + \frac{3}{5}c^5 + \frac{2}{3}c^6 - \frac{5}{7}c^7 + \frac{1}{4}c^8 \tag{3b}$$

$$\phi_{AA}(c) = -\frac{53}{840}c + \frac{2}{3}c^3 - \frac{5}{4}c^4 + \frac{6}{5}c^5 - c^6 + \frac{4}{7}c^7 - \frac{1}{8}c^8 \tag{3c}$$

$$\phi_{BB}(c)=\frac{23}{280}c-\frac{1}{2}c^4+\frac{2}{5}c^5+\frac{1}{7}c^7-\frac{1}{8}c^8 \tag{3d}$$

with $\omega=Z\left(\varepsilon_{AA}-\frac{\varepsilon_{AA}+\varepsilon_{BB}}{2}\right)$ is usually known as the interchange energy, Z is the coordination number, $\varepsilon_{ij}\ (i,j\equiv A,B)$ represent the energies for *ij*, *ii* and *jj* bonds and $\Delta\omega_{ij}$ are the interaction energy parameters. Equation (2) is employed to determine G_M^{XS} of the binary molten system having the existence of chemical complexes.

Equations (1) and (2) provide

$$\begin{aligned}\frac{G_M}{RT}=&\frac{\omega}{k_BT}\phi(c)+\frac{\Delta\omega_{AB}}{k_BT}\phi_{AB}(c)+\frac{\Delta\omega_{AA}}{k_BT}\phi_{AA}(c)+\frac{\Delta\omega_{BB}}{k_BT}\phi_{BB}(c)\\&+c\ln c+(1-c)\ln(1-c)\end{aligned} \tag{4}$$

which is the required equation for calculating the values of G_M as a function of concentration for a binary liquid alloy.

Activity is a very useful thermodynamic function which is directly ascertained from the experiment. The activity of the element i, *i.e.* $a_i\ (i\equiv A,B)$ of a binary molten system is given by [23]

$$\ln a_i=\frac{G_M}{RT}+\frac{(1-c_i)}{RT}\left(\frac{\partial G_M}{\partial c_i}\right)_{T,P,N} \tag{5}$$

Equations (4) and (5) yield

$$\begin{aligned}\ln a_A=&\frac{G_M}{RT}+(1-c)\left[\frac{\omega}{k_BT}\phi'(c)+\frac{\Delta\omega_{AB}}{k_BT}\phi'_{AB}(c)+\frac{\Delta\omega_{AA}}{k_BT}\phi'_{AA}(c)\right.\\&\left.+\frac{\Delta\omega_{BB}}{k_BT}\phi'_{BB}(c)+\ln\left(\frac{c}{1-c}\right)\right]\end{aligned}$$

or,

$$\begin{aligned}\ln a_A=&\frac{G_M}{RT}+(1-c)\left[\frac{\omega}{k_BT}(1-2c)\right.\\&+\frac{\Delta\omega_{AB}}{k_BT}\left(\frac{13}{420}+2c^2-6c^3+3c^4+4c^5-5c^6+2c^7\right)\\&+\frac{\Delta\omega_{AA}}{k_BT}\left(-\frac{53}{840}+2c^2-5c^3+6c^4-6c^5+4c^6-c^7\right)\\&\left.+\frac{\Delta\omega_{BB}}{k_BT}\left(\frac{23}{280}-2c^3+2c^4+c^6-c^7\right)+\ln\left(\frac{c}{1-c}\right)\right]\end{aligned} \tag{6}$$

and

$$\begin{aligned}\ln a_B=&\frac{G_M}{RT}-c\left[\frac{\omega}{k_BT}\phi'(c)+\frac{\Delta\omega_{AB}}{k_BT}\phi'_{AB}(c)+\frac{\Delta\omega_{AA}}{k_BT}\phi'_{AA}(c)\right.\\&\left.+\frac{\Delta\omega_{BB}}{k_BT}\phi'_{BB}(c)+\ln\left(\frac{c}{1-c}\right)\right]\end{aligned}$$

or,

$$\ln a_B = \frac{G_M}{RT} - c\left[\frac{\omega}{k_B T}(1-2c) + \frac{\Delta\omega_{AB}}{k_B T}\left(\frac{13}{420} + 2c^2 - 6c^3 + 3c^4 + 4c^5 - 5c^6 + 2c^7\right) + \frac{\Delta\omega_{AA}}{k_B T}\left(-\frac{53}{840} + 2c^2 - 5c^3 + 6c^4 - 6c^5 + 4c^6 - c^7\right) + \frac{\Delta\omega_{BB}}{k_B T}\left(\frac{23}{280} - 2c^3 + 2c^4 + c^6 - c^7\right) + \ln\left(\frac{c}{1-c}\right)\right] \tag{7}$$

The Equation (6) and (7) are utilized to compute the thermodynamic activities of the components A and B respectively of the binary molten system.

The entropy of mixing is believed to have numerous structural knowledge of the binary liquid systems, and it is difficult to measure experimentally. Thus, theoretical prediction of S_M is very important task. The entropy of mixing determines the equilibrium state of the system. The excess entropy of mixing is defined as [17]

$$S_M^{XS} = -\left[\frac{\partial G_M^{XS}}{T}\right]_P$$

Equations (2) and (3a)-(3c) provide

$$S_M^{XS} = -N\left[\frac{\partial\omega}{\partial T}\phi(c) + \frac{\partial}{\partial T}(\Delta\omega_{AB})\phi_{AB}(c) + \frac{\partial}{\partial T}(\Delta\omega_{AA})\phi_{AA}(c) + \frac{\partial}{\partial T}(\Delta\omega_{BB})\phi_{BB}(c)\right] \tag{8}$$

$$\frac{S_M^{XS}}{R} = -\left[\frac{1}{k_B}\frac{\partial\omega}{\partial T}\phi(c) + \frac{1}{k_B}\frac{\partial}{\partial T}(\Delta\omega_{AB})\phi_{AB}(c) + \frac{1}{k_B}\frac{\partial}{\partial T}(\Delta\omega_{AA})\phi_{AA}(c) + \frac{1}{k_B}\frac{\partial}{\partial T}(\Delta\omega_{BB})\phi_{BB}(c)\right] \tag{9}$$

Now, S_M of a binary molten system is given by

$$S_M = S_M^{XS} + S_M^{id}$$

or,

$$\frac{S_M^{XS}}{R} = -\left[\frac{1}{k_B}\frac{\partial\omega}{\partial T}\phi(c) + \frac{1}{k_B}\frac{\partial}{\partial T}(\Delta\omega_{AB})\phi_{AB}(c) + \frac{1}{k_B}\frac{\partial}{\partial T}(\Delta\omega_{AA})\phi_{AA}(c) + \frac{1}{k_B}\frac{\partial}{\partial T}(\Delta\omega_{BB})\phi_{BB}(c)\right] - \left[c\ln c + (1-c)\ln(1-c)\right] \tag{10}$$

The above equation determines S_M as a function of composition of the binary molten system. The enthalpy of mixing, H_M is one of the fortunate thermodynamic properties because H_M can be measured by calorimetric experiments. It gives the information about the nature of bonding between the constituents of a liquid system. Therefore, theoretical analysis of H_M for a binary molten alloy is an interesting part of the investigation. Now, H_M is expressed as [23]

$$H_M = G_M + TS_M$$

Using Equations (4) and (10), one can obtain

$$\frac{H_M}{R} = \left[\frac{\omega}{k_B T} - \frac{1}{k_B}\frac{\partial\omega}{\partial T}\right]c(1-c) + \left[\frac{\Delta\omega_{AB}}{k_B T} - \frac{1}{k_B}\frac{\partial(\Delta\omega_{AB})}{\partial T}\right]\phi_{AB}(c) + \left[\frac{\Delta\omega_{AA}}{k_B T} - \frac{1}{k_B}\frac{\partial(\Delta\omega_{AA})}{\partial T}\right]\phi_{AA}(c) + \left[\frac{\Delta\omega_{BB}}{k_B T} - \frac{1}{k_B}\frac{\partial(\Delta\omega_{BB})}{\partial T}\right]\phi_{BB}(c) \tag{11}$$

The concentration dependence of the enthalpy of mixing, H_M of a binary molten system can be analysed.

2.2. Structural Properties *i.e.* Concentration Fluctuations, $S_{cc}(0)$ and Short-Range Order (SRO) Parameter, α_1

The microscopic function *i.e.* $S_{cc}(0)$ has appeared as a very interesting parameter to visualize the character of a microscopic structure of a molten binary system. The $S_{cc}(0)$ may be expressed as [23]-[25]

$$S_{cc}(0) = Nk_B T\left(\frac{\partial^2 G_M}{\partial c^2}\right)^{-1}_{T,P,N} \tag{12a}$$

$$S_{cc}(0) = (1-c)a_A\left(\frac{\partial a_A}{\partial c}\right)^{-1}_{T,P,N} = ca_B\left(\frac{\partial a_B}{\partial(1-c)}\right)^{-1}_{T,P,N} \tag{12b}$$

where, a_A and $a_B$represent the activities of A and B respectively of a binary system. It should be noted that $\left(\frac{\partial^2 G_M}{\partial c^2}\right)^{-1}_{T,P,N}$ determines the stability of a binary solution. The values of $S_{cc}(0)$ determined from Equation (12b) on utilizing the experimentally measured values of a_A and a_B are referred to as the experimental data of $S_{cc}(0)$. For ideal alloys,

$$G_M^{id} = RT\sum_i c_i \ln c_i \left(i \equiv A, B\right) \tag{13}$$

This readily leads to an equation for the ideal concentration fluctuations *i.e.*

$$S_{cc}^{id}(0) = c(1-c) \tag{14}$$

The departure of $S_{cc}(0)$ from $S_{cc}^{id}(0)$ is very important to explain the nature of ordering in the binary systems [26]. It is pointed out that $S_{cc}(0) > S_{cc}^{id}(0)$, leads to ordered alloys and $S_{cc}(0) > S_{cc}^{id}(0)$ represents the segregating alloys [23].

Using Equations (4) and (12a), one can obtain

$$S_{cc}(0) = \frac{c(1-c)}{1 + \frac{\phi(c)}{k_B T}\left[-2\omega + \Delta\omega_{AB}\phi''_{AB} + \Delta\omega_{AA}\phi''_{AA} + \Delta\omega_{BB}\phi''_{BB}\right]} \tag{15}$$

where,

$$\phi''_{AB} = \frac{\partial^2}{\partial c^2}\phi_{AB}(c) = 4c - 18c^2 + 12c^3 + 20c^4 - 30c^5 + 14c^6 \tag{16}$$

$$\phi''_{AA} = \frac{\partial^2}{\partial c^2}\phi_{AA}(c) = 4c - 15c^2 + 24c^3 - 30c^4 + 24c^5 - 7c^6 \tag{17}$$

$$\phi''_{BB} = \frac{\partial^2}{\partial c^2}\phi_{AA}(c) = -6c^2 + 8c^3 + 6c^5 - 7c^6 \tag{18}$$

The short-range order (SRO) parameter, α_1 in the first nearest- neighbour shell of a binary mixture [27] [28] may be expressed as

$$\alpha_1 = \frac{(S-1)}{S(Z-1)+1} \quad \text{with} \quad S = \frac{S_{cc}(0)}{S_{cc}^{id}} \tag{19}$$

where, Z represents the coordination number. Equation (19) is used for the theoretical prediction of α_1 for a binary molten system.

2.3. Transport Property *i.e.* Diffusivity Ratio, $\frac{D_M}{D_{id}}$

The atomic diffusivity is a key transport property that helps to explain the microscopic mechanism of mixing in binary melt. It describes the rate at which constituent atoms migrate within the melt and therefore strongly influenced by the interatomic interactions and local structural arrangements.

For a binary molten system, the ratio of diffusivity can be expressed in terms of $S_{cc}(0)$ thermodynamic quantities as given in [23] [29]

$$\frac{D_M}{D_{id}} = \frac{S_{cc}^{id}(0)}{S_{cc}(0)} \tag{20}$$

here, D_M signifies the mutual diffusion coefficient for a metallic melt, whereas D_{id} corresponds to the ideal intrinsic diffusion coefficient. The expression for the ideal intrinsic diffusion coefficient is given by

$$D_{id} = c_A D_B + c_B D_A \tag{21}$$

In this expression, D_i (with $i \equiv A, B$) signifies the self-diffusion coefficient of component *i*. Equation (20) suggests that the binary molten alloys can exhibit either segregating alloys or chemical ordering depending on the relative magnitude of relevant diffusion ratio. A value of $\frac{D_M}{D_{id}}$ greater than unity signifies the tendency towards segregation i.e predominance of like atoms interactions (A-A or B-B) whereas the value of $\frac{D_M}{D_{id}}$ less than unity indicates ordering nature *i.e.* the predominance of unlike (A-B) atoms interactions in the melt [23].

3. Results and Discussions

3.1. Thermodynamic Properties *i.e.* G_M^{XS}, G_M, Activity, H_M, S_M of Bi-Tl Melts at 750 K

From Equations (2) and (4), the thermodynamic behaviour of liquid Bi-Tl at 750 K was analysed by comparing theoretical and experimental [1] values of the excess Gibbs free energy of mixing, $\frac{G_M^{XS}}{RT}$ and free energy of mixing G_M/RT, as a function

of Bi mole fraction (C_{Bi}). The best values of the interaction parameters to satisfy the thermodynamic properties in Equation (2) and (4) are evaluated as suggested earlier [17] [21] [30] the values are

$$\frac{\omega}{k_B T} = -2.660;\ \frac{\Delta\omega_{AB}}{k_B T} = 0.020;\ \frac{\Delta\omega_{AA}}{k_B T} = 9.030 \text{ and } \frac{\Delta\omega_{AA}}{k_B T} = -4.700$$

Figure 1 shows that the curves of G_M^{XS} and G_M are asymmetric with respect to the composition and having minima *i.e.* −0.789 (Theory) and −0.782 (Experiment) for $\frac{G_M^{XS}}{RT}$, and −1.462 (Theory) and −1.455 (Experiment) for $\frac{G_M^{XS}}{RT}$ both at $C_{Bi} = 0.4$. The thermodynamic analysis of Bi-Tl melts at 750 K for G_M and G_M^{XS}, exhibits the negative values over the entire composition range $0.1 \le C_{Bi} \le 0.9$ which confirms the attractive interactions dominate between Bi and Tl atoms in the liquid phase. This indicates that the mixing is thermodynamically favourable at 750 K. Such attractive interactions promote short-range ordering in the alloy and stabilise the mixed liquid state. Again, the magnitude of $\frac{G_M}{RT}$ justifies that Bi-Tl system at 750 K is a feebly interacting system [24].

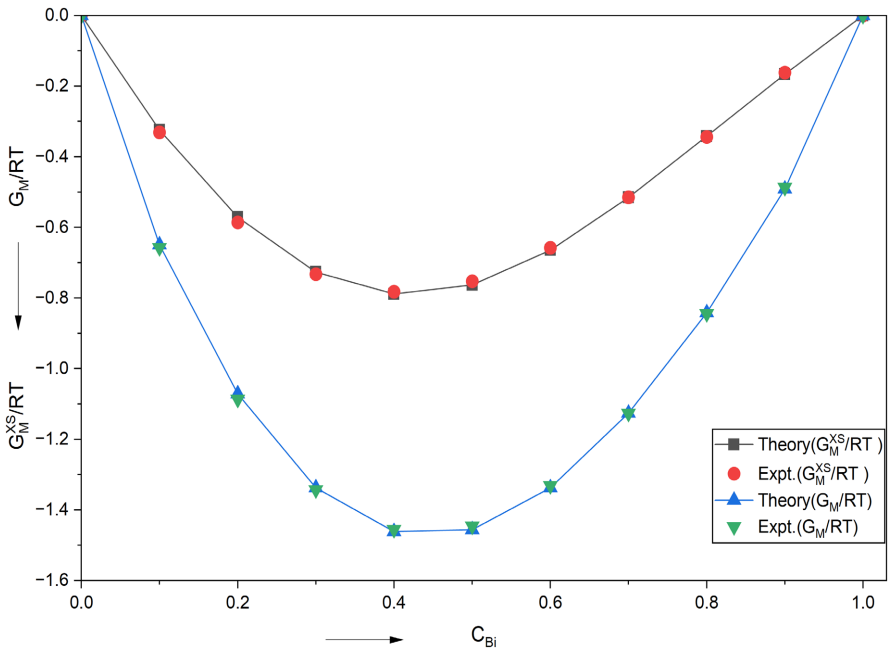


Figure 1. The $\frac{G_M^{XS}}{RT}$ and $\frac{G_M}{RT}$ versus C_{Bi}, for Bi-Tl melt at 750 K.

Furthermore, the asymmetric shape of the curve around the composition C_{Bi} = 0.4 indicates that the maximum interaction between the components occurs near C_{Bi} = 0.4. The small difference between theoretical and experimental values confirms that the theoretical model accurately describes the thermodynamic quantities of Bi-Tl alloy at 750 K. The excellent agreement

between theoretical predictions and experimental data confirms the suitability in the framework of QLM model.

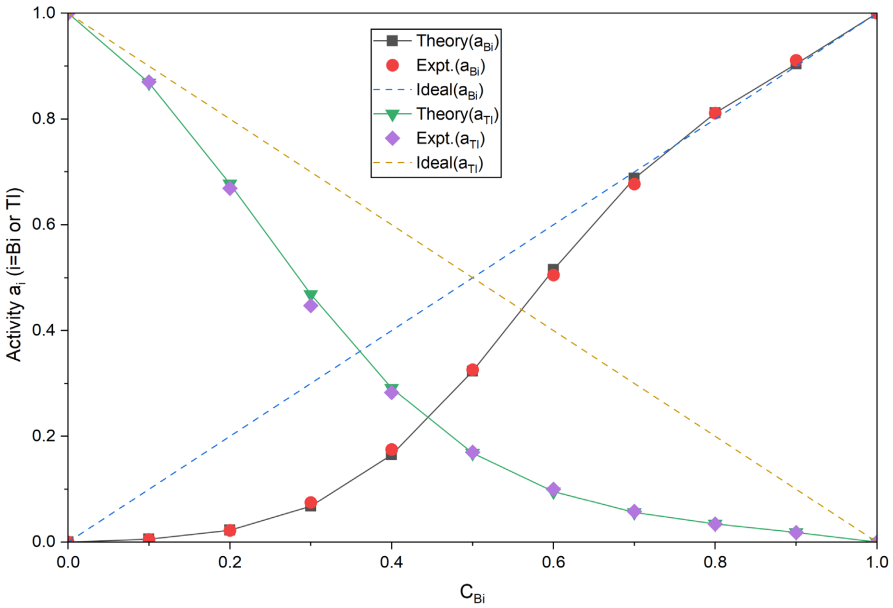


Figure 2. a_{Bi} and a_{Tl} versus C_{Bi} for Bi-Tl melt at 750 K.

The activity of Bi (a_{Bi}) and Tl (a_{Tl}) in liquid Bi-Tl at 750 K are determined theoretically equations (6) and (7) respectively and compared with experimental [1] values and ideal solution behaviour. In **Figure 2**, a_{Bi} shows significant negative deviation from ideal behaviour in the composition region $0.0 \leq C_{Bi} \leq 0.7$ and beyond $C_{Bi} = 0.75$ the deviation becomes small positive while a_{Tl} exhibits significant negative departure from ideality over the entire composition range 0.1 to 0.9. This confirms the heterotopic bonding in the liquid alloy [13] *i.e.* Bi-Tl system at 750 K is an ordered alloy. Again, the largest deviations for a_{Bi} and a_{Tl} *i.e.* 0.174 and 0.330 respectively occur near $C_{Bi} = 0.5$, indicating the maximum interactions strength at the equiatomic composition and short-range ordering in the melt. These findings confirm that the liquid Bi-Tl at 750 K is a chemically ordered melt. The agreement between theoretical and experimental data of the activities of Bi and Tl for Bi-Tl melts at 750 K validates the evaluated values of energy parameters because the activates are experimentally measured [23].

The equations (10) and (11) show that the thermodynamic quantities S_M and H_M depend on the temperature derivatives of the interaction parameters *i.e.* $\frac{\partial\omega}{\partial T}$, $\frac{\partial(\Delta\omega_{AB})}{\partial T}$, $\frac{\partial(\Delta\omega_{AA})}{\partial T}$ and $\frac{\partial(\Delta\omega_{BB})}{\partial T}$ whose values were optimized by the successive approximation [21] [30] on employing the experimental data of S_M in equation (10). The optimized values are $\frac{\partial\omega}{\partial T} = -0.102k_B$; $\frac{\partial(\Delta\omega_{AB})}{\partial T} = -0.902k_B$; $\frac{\partial(\Delta\omega_{AA})}{\partial T} = -1.403k_B$ and $\frac{\partial(\Delta\omega_{BB})}{\partial T} = -3.003k_B$

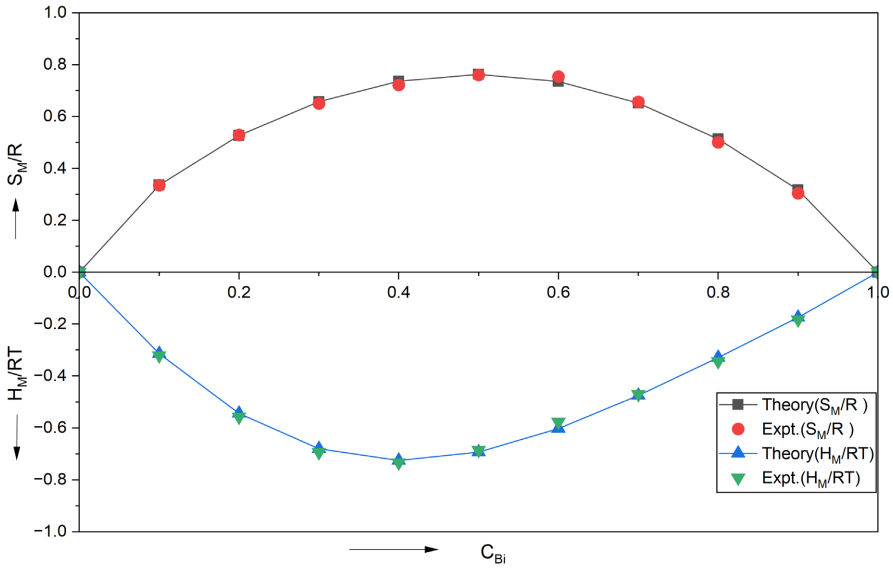


Figure 3. $\frac{S_M}{R}$ and $\frac{H_M}{RT}$ versus C_{Bi} for Bi-Tl melt at 750 K.

The entropy of mixing, S_M of liquid Bi-Tl at 750 K is calculated theoretically from equation (10) and compared with experimental findings [1] over the entire composition range in **Figure 3**. The result demonstrates very good agreement between theory and experiment, confirming the reliability of the thermodynamic description of the system. **Figure 3** shows that the entropy of mixing is zero at pure component limit *i.e.* $c = 0$ and $c = 1$, as expected for unmixed system. With increasing Bi components, S_M/R increases smoothly and becomes maximum 0.763 (Theory) and 0.760(Experiment) both at the equiatomic composition *i.e.* $C_{Bi} = 0.5$. The entropy curve is symmetric and the theoretical and experimental values differ only slightly. The small deviations at intermediate compositions arise from minor short range ordering effects in the melt. Therefore, at 750 K the thermodynamic stability of the liquid Bi-Tl alloy is mainly due to favourable interaction energy rather than entropy effect. The close correspondence confirms the adequacy in the framework of theoretical model QLM.

Similarly, the enthalpy of mixing, H_M of liquid Bi-Tl at 750 K is evaluated as a function of Bi- mole fraction from equation (11) and the theoretical data are compared with experimental [1] data in **Figure 3**. Obviously, an excellent agreement between calculated and measured [1] values is noticed over the entire range of composition. The minimum value of enthalpy *i.e.* H_M/RT are −0.725 (Theory) and −0.734 (Experiment) both at near $C_{Bi} = 0.4$. This shows the attractive interaction between Bi and Tl atoms about $C_{Bi} = 0.4$ and Bi-Tl system at 750 K possesses ordering character. The close agreement between theoretical and experimental values demonstrates that the applied theoretical model QLM effectively describes the thermodynamic behaviour of Bi-Tl molten alloys at 750 K.

3.2. Structural Properties *i.e.* $S_{cc}(0)$ and α_1

The concentration fluctuations, $S_{cc}(0)$ for Bi-Tl melts at 750 K computed using

Equations (15)-(18) relative to the composition of Bi is represented in **Figure 4** along with the experimental data [5] as well as $S_{cc}(0)$ ideal. It is clear that both theoretical and experimental [1] results exhibit close agreement with having maxima 0.1591 (Theory) and 0.1457 (Experiment) occurring at $C_{Bi} = 0.8$ with an error of about 9.2%. Importantly, the values of $S_{cc}(0)$ are consistently lower than the corresponding ideal values in the composition range, $0.0 \le C_{Bi} \le 0.8$ and beyond $C_{Bi} = 0.8$ $S_{cc}(0)$ becomes slightly greater than $S_{cc}^{id}(0)$. This indicates that Bi-Tl melt at 750 K is an ordered alloy in the region $0.0 \le C_{Bi} \le 0.8$ and the large negative deviation of $S_{cc}(0)$ from the ideal values refers to the tendency of complex formation in Bi-Tl melts at 750 K. Again, Bi-Tl system at 750 K exhibits slight segregation in the higher concentration region of Bi *i.e.* $C_{Bi} > 0.8$, this may be due to the fact that activity of Bi exhibit positive deviation from linearity in the higher concentration region.

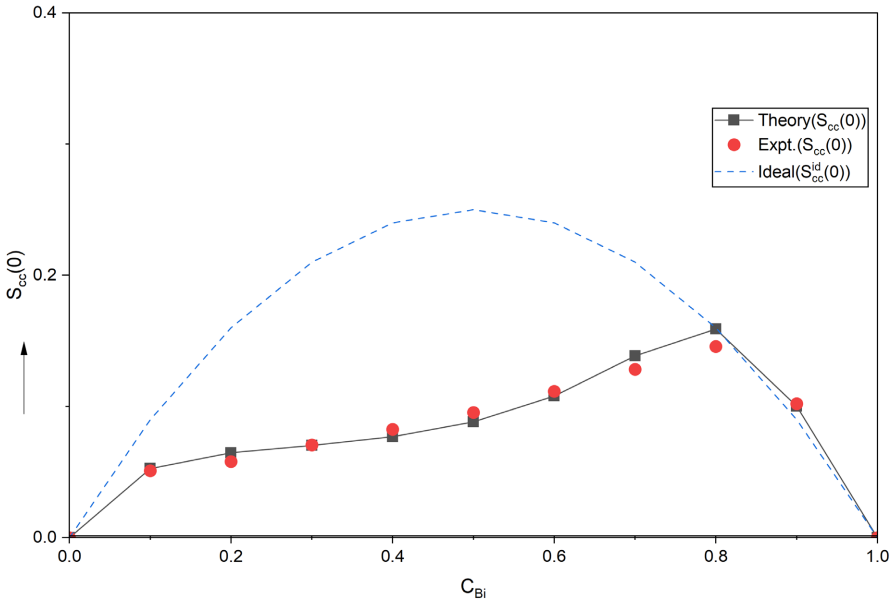


Figure 4. $S_{cc}(0)$ versus C_{Bi} for Bi-Tl melt at 750 K.

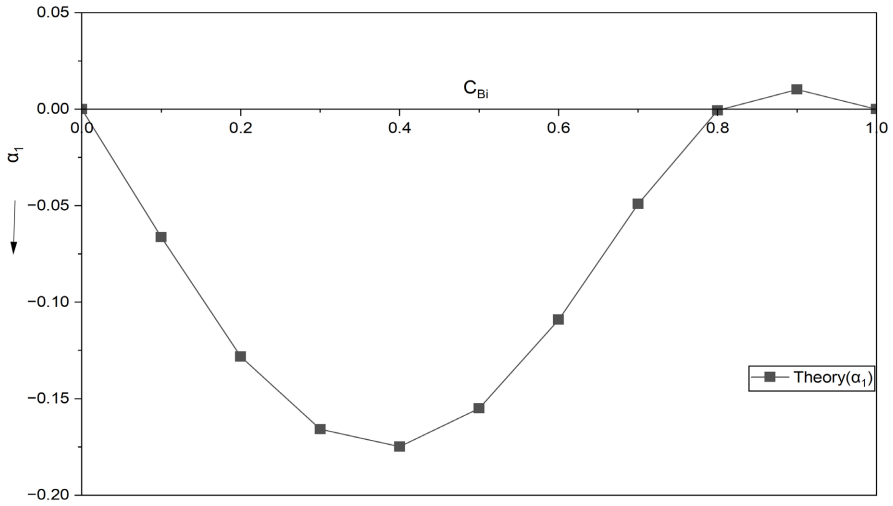


Figure 5. α_1 versus C_{Bi}, for Bi-Tl melt at 750 K.

The strong correlation between theoretical predictions and experimental measurements derived from activity data [1] demonstrates the reliability of thermodynamic model in describing the ordering behaviour and complex forming of the alloy at elevated temperature. Overall, the result suggests that Bi_3Tl_2 at 750 K is thermodynamically stable and exhibit significant non-ideal solution behaviour driven by interatomic interactions [17] [18].

The SRO, α_1 describes the local atomic arrangement in liquid alloy [27] [28]. The value of $\alpha_1 = 0$ indicates a random distribution of atoms. Positive values *i.e.* $\alpha_1 > 0$ show the segregation where like atoms prefer to cluster together, while negative values *i.e.* $\alpha_1 < 0$ show chemical ordering, meaning unlike atoms preferentially occupy nearest neighbour sites.

Figure 5 shows SRO, α_1 [27] [28] as a function of Bi concentration C_{Bi} is negative in most of the composition range *i.e.* $c = 0.1$ to 0.8 and positive at $C_{Bi=}0.9$ as calculated from equation (19) on using $Z = 10$. Since no experimental data of α_1 are available for Bi-Tl melts hence direct comparison is not possible. The magnitude of α_1 increases with Bi composition, reaching a minimum value of -0.1748 at $C_{Bi} = 0.4$ and beyond $C_{Bi} = 0.4$ it decreases gradually. The negative values of α_1 indicate a preference for unlike atom pairs (Bi-Tl) over like pairs (Bi-Bi or Tl-Tl). At $C_{Bi=}0.9$ the value becomes positive ($\alpha_1 > 0$) indicates slight segregation tendency in the Bi rich region. This confirms that the alloy exhibits a tendency towards chemical short-range ordering but the system favour segregation in the rich composition *i.e.* $C_{Bi=}0.9$ at 750 K.

3.3. Transport Properties *i.e.* $\frac{D_M}{D_{id}}$

The diffusivity ratio $\frac{D_M}{D_{id}}$ calculated [29] from equation (20) for Bi-Tl melt at

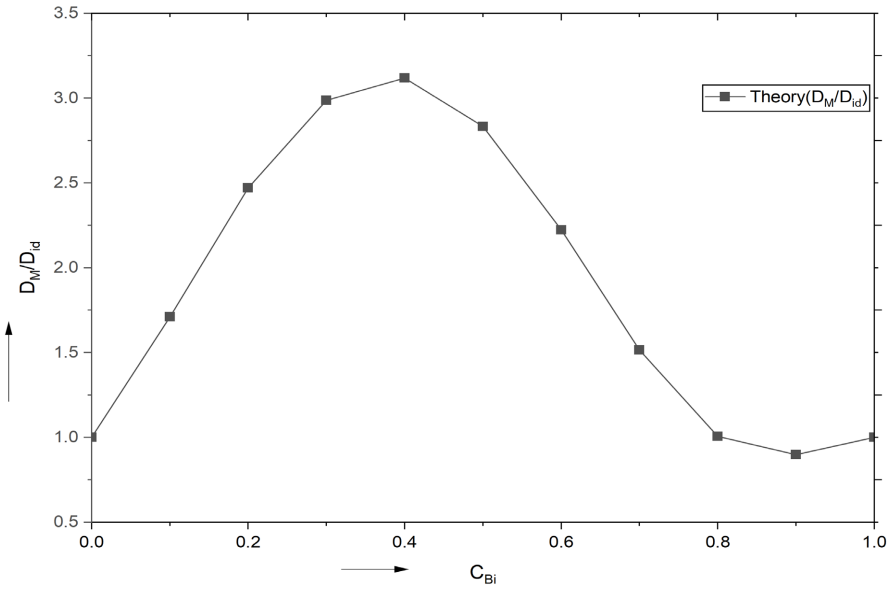


Figure 6. $\frac{D_M}{D_{id}}$ versus C_{Bi}, for Bi-Tl melt at 750 K.

750 K is greater than unity over the entire intermediate composition range, reaching a maximum of 3.1187 at $C_{Bi=}$ 0.4. This behaviour confirms enhanced diffusion due to attractive interatomic interactions and chemical ordering effect. As shown in **Figure 6** the results are consistent with the thermodynamic and structural properties of the alloy, indicating non-ideal but stable melt behaviour. Again, no comparison with experimental data is possible as there is no experimental value available in the literature.

4. Conclusions

The Bi-Tl melt at 750 K exhibits pronounced non-ideal behavior governed by strong heteroatomic interactions. The negative Gibbs free energy and enthalpy of mixing over the entire composition range confirm spontaneous and exothermic alloy formation. The entropy of mixing shows a symmetric variation with a maximum at intermediate composition, indicating partial suppression of configurational randomness due to chemical ordering.

The negative deviations of the activities of Bi and Tl, and Scc(o) from ideal mixing, the negative value of a_1 as well as $\frac{D_M}{D_{id}}$ is greater than 1, reveal a clear tendency toward unlike-atoms (Bi-Tl) association as nearest neighbors to form the chemical complexes. However, the formation of Bi_3Tl_2 complexes is theoretically not predicted. Thus, the quasi-lattice model provides a consistent description of the thermodynamic, structural, and transport behavior of the Bi-Tl melt at 750 K. Nonetheless, its applicability may be limited for segregating systems dominated by like-atom interactions.

Author Contributions

Conceptualization, I. S. Jha, A. K. Pandey and J. Mandal; methodology, Prakash Ranjan Deen; validation, I. S. Jha, and A. K. Pandey; formal analysis; Prakash Ranjan Deen and Soni Kumari; investigation, Prakash Ranjan Deen; writing original draft preparation, Prakash Ranjan Deen and Soni Kumari; writing-review and editing, A. K. Pandey and J. Mandal; visualization, I. S. Jha; supervision, A. K. Pandey and J. Mandal. All authors have read and agreed to published version of the manuscript.

Conflicts of Interest

All the authors declare no conflict of interest regarding the publication of this paper.

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