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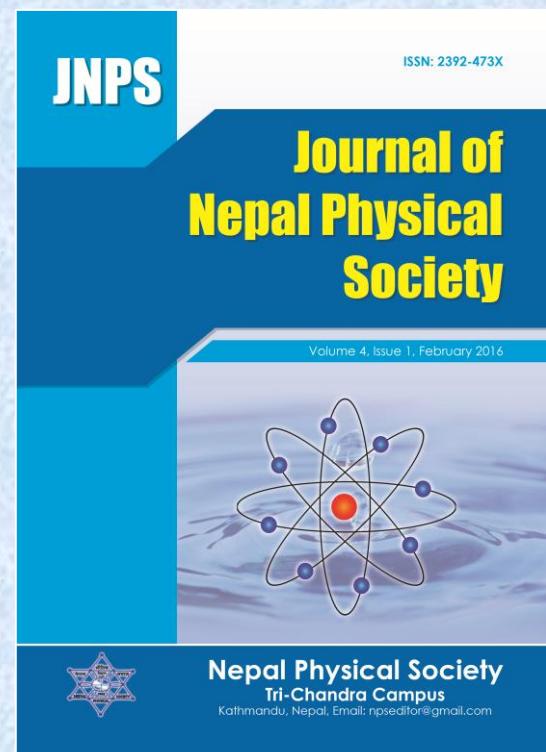
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Theoretical Modeling to Predict the Thermodynamic, Structural, Surface and Transport Properties of the Liquid Tl–Na Alloys at different Temperatures

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ABSTRACT

Theoretical modeling equations are developed by extending regular associated solution model to predict the thermodynamic and structural properties of the liquid Tl–Na alloys at higher temperatures. The thermodynamic properties have been predicted by computing activities of unassociated monomers (a_{Ti} and a_{Na}) and free energy of mixing (G_M) at temperatures 673 K, 773 K, 873 K and 973 K. The structural properties have been predicted by computing concentration fluctuation in long wavelength limit ($S_{CC}(0)$), short range order parameter (α_1) and ratio of mutual to intrinsic diffusion coefficients (D_M/D_{id}) at aforementioned temperatures. These properties have been then correlated with the modified Butler's model to predict the surface properties, such as surface concentrations of free monomers (X_{Ti}^S and X_{Na}^S) and surface tension (σ) of the alloy at above mentioned temperatures.

Keywords: Modeling equations, Thermodynamic properties, Modified Butler's model, Surface concentrations.

INTRODUCTION

Alloys differ in the physical as well as chemical properties than that of its constituent atoms of mixture. They possess light weight, high melting point, high temperature resistance, resistance to corrosion and oxidation, etc. which makes them suitable to be used in military, medical, aeronautics and all most entire metallurgical designing of equipments. The alloys are synthesized and characterized from the liquid state near the melting temperature of their ingredient atoms. Eventually, the study and prediction of the energetic of the initial melt is of fundamental interest of most modern day researches. Moreover, the study of the mixing behaviours of the initial melt at different temperatures experimentally have many constraints, such as difficulty in controlling temperatures, tedious, time consuming, high economical costs and developing new devices having high temperature and corrosion resistances. These difficulties have been to some extent resolved by theoretician by developing different modeling equations (Flory, 1942; Jordan, 1970; Bhatia & Hargrove, 1974; Lele & Ramchandrarao, 1981; Ruppertsberg & Reiter, 1982; Hoshino, 1983; Young, 1992; Singh & Sommer, 1992; Budai,

Benko & Kapta, 2005; Kapta, 2008, 2015; Adhikari, Singh & Jha, 2010; Adhikari, 2011; Yadav, Jha & Adhikari, 2014) to study the mixing behaviours of the liquid alloys at the melting temperatures and interpolating/extrapolating these results at different elevated temperatures. In the light of such fundamental importance, we have extended regular associated solution model (Jordan, 1970; Lele & Ramchandrarao, 1981; Adhikari, Singh & Jha, 2010; Adhikari, 2011; Yadav, Jha & Adhikari, 2014) and employed it to predict the thermodynamic, structural and surface properties of the liquid Tl–Na alloys at higher temperatures (Yadav *et al.*, 2016).

According to regular associated solution model, when atoms A (=Tl) and B (=Na) are mixed at a temperature near to their melting point, there is favourable associations of the types AA, BB and AB. These associations are termed as "pseudomolecules" or "clusters" (Lele & Ramchandrarao, 1981; Adhikari, 2011; Yadav, Jha & Adhikari, 2014). The associations between the like atoms (AA and BB) are termed as demixing (segregating) whereas of the unlike atoms (AB) is termed as mixing (ordering) of the liquid alloys. Additionally, it is assumed that there appear

unequal interactions between the complex (AB) and free monomers (A and B) in the liquid state. The expressions for the different thermodynamic and structural functions are derived on this basis. Yadav *et al.* (2014) have mentioned the importance of choosing the aforementioned alloy system for study. In this work, we intend to predict the thermodynamic and structural properties of Tl–Na liquid alloys at higher temperatures 673 K, 773 K, 873 K and 973 K by assuming the complex TlNa at 673 K (Yadav, Jha & Adhikari, 2015) on the basis of extended regular associated solution model. The thermodynamic properties have been then correlated with the modified Butler model (Kaptay, 2008, 2015; Yadav *et al.*, 2016) to predict the surface properties of the concerned system at different temperatures.

The theory containing the different thermodynamic functions is presented in the Section 2, results and discussion is highlighted in the Section 3 and the conclusions are outlined in the Section 4.

THEORY

Thermodynamic Properties:

Let one mole of the liquid solution consists of n_1 atoms of atom A (=Tl) and n_2 atoms of B (=Na). There is then formation of the complex of the type $A_\mu B$ ($\mu A + B \rightleftharpoons A_\mu B$), where μ is a small integer whose value is chosen from the complex formation concentration ($=\mu/(\mu + 1)$) and $\mu = 1$ for our study (Yadav, Jha & Adhikari, 2015). If x_A , x_B and $x_{A_\mu B}$ are the true mole fractions of unassociated atoms Tl, Na and the complex TlNa in the initial melt, then they can be expressed as (Lele & Ramchandrarao, 1981)

$$x_A = x_1 - \mu x_2 x_{A_\mu B} \text{ and}$$

$$x_B = x_2 - (1 - \mu x_2) x_{A_\mu B} \quad (1)$$

where x_1 and x_2 are the gross mole fractions of A and B in the melt.

According to the regular associated solution model $x_1\gamma_1 = x_A\gamma_A$ and $x_2\gamma_2 = x_B\gamma_B$, where γ_1 and γ_2 are the gross activity coefficients of components 1 and 2 respectively. It can thus be shown that

$$\ln\gamma_1 = \ln\gamma_A + \ln\left(\frac{x_A}{x_1}\right) \quad (2a)$$

$$\text{and, } \ln\gamma_2 = \ln\gamma_B + \ln\left(\frac{x_B}{x_2}\right) \quad (2b)$$

According to Jordan, (Jordan, 1970) the activity coefficients of monomers γ_A , γ_B and complex $\gamma_{A_\mu B}$ can be represented in terms of pairwise interaction energies as

$$\begin{aligned} RT \ln\gamma_A = \\ x_B^2 \omega_{12} + x_{A_\mu B}^2 \omega_{13} + x_B x_{A_\mu B} (\omega_{12} - \omega_{23} + \omega_{13}) \end{aligned} \quad (3a)$$

$$RT \ln\gamma_B = x_{A_\mu B}^2 \omega_{23} + x_A^2 \omega_{12} + x_A x_{A_\mu B} (\omega_{23} - \omega_{13} + \omega_{12}) \quad (3b)$$

$$RT \ln\gamma_{A_\mu B} = x_A^2 \omega_{13} + x_B^2 \omega_{23} + x_A x_B (\omega_{13} - \omega_{12} + \omega_{23}) \quad (3c)$$

where ω_{12} , ω_{13} and ω_{23} represents the pairwise interaction energies for the species A, B; A, $A_\mu B$ and B, $A_\mu B$ respectively. T and R represent absolute temperature and universal real gas constant respectively.

On solving Equations (3a) and (3b), we obtain

$$\frac{\omega_{13}}{RT} = \frac{x_B \ln\left(\frac{\alpha_2}{x_B}\right) + (1 - x_B) \ln\left(\frac{\alpha_1}{x_A}\right) - x_B (1 - x_B) \frac{\omega_{12}}{RT}}{x_{A_\mu B}^2} \quad (4)$$

$$\frac{\omega_{23}}{RT} = \frac{x_A \ln\left(\frac{\alpha_1}{x_A}\right) + (1 - x_A) \ln\left(\frac{\alpha_2}{x_B}\right) - x_A (1 - x_A) \frac{\omega_{12}}{RT}}{x_{A_\mu B}^2} \quad (5)$$

where $\alpha_1 = x_1\gamma_1$ and $\alpha_2 = x_2\gamma_2$ are activities of components 1 and 2 respectively.

Following Lele and Ramchandrarao, the equilibrium constant for the reaction $A_\mu B \rightleftharpoons \mu A + B$ can given by following equation (Lele & Ramchandrarao, 1981)

$$k = \frac{x_A^\mu x_B \gamma_A^\mu \gamma_B}{x_{A_\mu B} \gamma_{A_\mu B}} \quad (6)$$

Solving Equations (3) and (6), the relation for the equilibrium constant can be obtained as

$$\begin{aligned} \ln k = \ln\left(\frac{x_A^\mu x_B}{x_{A_\mu B}}\right) + \frac{\omega_{12}}{RT} + \frac{\omega_{12}}{RT} [\mu x_B (1 - x_A) + x_A] + \frac{\omega_{13}}{RT} [\mu x_{A_\mu B} (1 - x_A) - x_A] + \frac{\omega_{23}}{RT} [x_{A_\mu B} (1 - \mu x_B) - x_B] \end{aligned} \quad (7)$$

The pairwise interaction energies, the equilibrium constants and the activity coefficients at infinite dilution for $\mu = 1$ can be related as (Lele & Ramchandrarao, 1981)

$$\ln\gamma_1^0 = \frac{\omega_{12}}{RT} + \left[1 - \left(1 + k \exp\frac{\omega_{23} - \omega_{12}}{RT}\right)^{-1}\right] \quad (8a)$$

$$\ln\gamma_2^0 = \frac{\omega_{12}}{RT} + \left[1 - \left(1 + k \exp\frac{\omega_{13} - \omega_{12}}{RT}\right)^{-1}\right] \quad (8b)$$

where γ_1^0 and γ_2^0 are the activity coefficients at zero concentrations of the free monomers A and B respectively. On solving Equations (4), (5) and (7), we obtain

$$\ln k + \frac{\omega_{13}}{RT} = \left(\frac{1+x_A}{x_{A_\mu B}} \right) \ln \left(\frac{x_1}{x_A} \right) + \frac{x_B}{x_{A_\mu B}} \left[\ln \left(\frac{x_1}{x_A} \right) - \frac{\omega_{12}}{RT} \right] + \ln \left(\frac{a_1^\mu a_2}{x_{A_\mu B}} \right) \quad (9a)$$

$$= \ln \gamma_1^0 - \ln [1 - \gamma_2^0 \exp(-\omega_{12}/RT)] \quad (9b)$$

The expression for the complex at equiatomic composition i.e., at $x_1 = x_2 = 0.5$; $x_A = x_B$ can be written as

$$x_{A_\mu B} = \frac{\ln(\gamma_2/\gamma_1)_{x_1=x_2=0.5}}{\ln \left[\frac{\gamma_1^0}{\gamma_2^0} \cdot \frac{1-\gamma_2^0 \exp(-\frac{\omega_{12}}{RT})}{1-\gamma_1^0 \exp(-\frac{\omega_{12}}{RT})} \right]} \quad (10)$$

The mole fraction of the complex and the interaction energy ω_{12} are simultaneously obtained by solving equations 9 and 10 by an iterative procedure. Once the mole fractions and the model parameters are obtained, the thermodynamic and the microscopic structural properties of both of the liquid alloys can be obtained by the similar procedure as given above.

The free energy of mixing (G_M) is given as (Lele & Ramchandrarao, 1981)

$$G_M = \frac{1}{1+\mu x_{A_\mu B}} RT \left[\left(x_A x_B \frac{\omega_{12}}{RT} + x_A x_{A_\mu B} \frac{\omega_{13}}{RT} + x_B x_{A_\mu B} \frac{\omega_{23}}{RT} \right) + (x_A \ln x_A + x_B \ln x_B + x_{A_\mu B} \ln x_{A_\mu B}) + x_{A_\mu B} \ln k \right] \quad (11)$$

Structural Properties:

The study of microscopic structural properties helps to understand the nature of local arrangements between the atoms in the nearest neighbourhood in the liquid state. It also helps in explaining miscibility or immiscibility of the constituents atoms in the melt. The concentration fluctuation in the long wavelength limit ($S_{CC}(0)$) is related with free energy of mixing (G_M) by the following standard thermodynamic relations

$$S_{CC}(0) = RT \left(\frac{\partial^2 G_M}{\partial x_1^2} \right)_{T,P}^{-1} \quad (12a)$$

$$S_{CC}(0) = x_2 \alpha_1 \left(\frac{\partial \alpha_1}{\partial x_1} \right)_{T,P}^{-1} = x_1 \alpha_2 \left(\frac{\partial \alpha_2}{\partial x_2} \right)_{T,P}^{-1} \quad (12b)$$

The expression for the concentration fluctuation in the long-wavelength limit ($S_{CC}(0)$) can be obtained by using equation 11 in equations 12 (a) and 12 (b) as

$$S_{CC}(0) = 1 / \left[\left(\frac{1}{1+\mu x_{A_\mu B}} \right) \left\{ \frac{2}{RT} \left(x'_A x'_B w_{12} + x'_A x'_{A_\mu B} w_{13} + x'_B x'_{A_\mu B} w_{23} \right) + \left(\frac{x_A'^2}{x_A} + \frac{x_B'^2}{x_B} + \frac{x_{A_\mu B}^2}{x_{A_\mu B}} \right) \right\} \right] \quad (13)$$

Here, $\frac{\partial^2 G_M}{\partial x_1^2} > 0$ for $\frac{\partial G_M}{\partial x_1} = 0$. The prime denotes the differentiations with respect to concentrations, and x'_A and x'_B are obtained by using Equation (1). $x'_{A_\mu B}$ is obtained using equation 7 by using the condition $\frac{d \ln k}{dx_1} = 0$ (Adhikari, Singh & Jha, 2010; Adhikari, 2011; Yadav, Jha & Adhikari, 2014). The factor $(1 + \mu x_{A_\mu B})^{-1}$, which appears as a coefficient of all terms containing x_A , x_B and $x_{A_\mu B}$ in equations 11 and 13, is a result of change in the basis for expressing the mole fractions of species A, B and $A_\mu B$ from that used for x_1 and x_2 .

The concentration fluctuation in long wavelength limit ($S_{CC}(0)$) has been developed as an important tool to understand the nature of atomic ordering in the binary liquid alloys. At a given concentration, if $S_{CC}(0) < S_{CC}^{id}(0)$, then ordering (unlike atoms pairing) is expected and if $S_{CC}(0) > S_{CC}^{id}(0)$, then segregation (like atoms pairing) is expected, where $S_{CC}^{id}(0) = x_1 x_2$. The experimental values of $S_{CC}(0)$ can be obtained from equation 13 (b).

The degree of local ordering in such liquid systems can be studied by estimating Warren-Cowley short range order parameter (α_1) with the knowledge of ($S_{CC}(0)$) (Bhatia & Hargrove, 1974; Singh, 1987; Novakovic, 2010). The expression for α_1 in terms of $S_{CC}(0)$ is given as

$$\alpha_1 = \frac{S-1}{S(Z-1)+1}$$

where, $S = \frac{S_{CC}(0)}{S_{CC}^{id}(0)}$ and

$$S_{CC}^{id}(0) = x_1 x_2 \quad (14)$$

where Z is the coordination number and $Z=10$ is taken for our calculation. We note that varying the

value of Z does not have any effect on the position of the minima of α_1 ; the effect is to vary the depth while the overall features remains unchanged.

The expression for the ratio of mutual to intrinsic diffusion coefficients in terms of $S_{CC}(0)$ can be given as (Darken & Gurry, 1953; Singh & Sommer, 1998) :

$$\frac{D_M}{D_{id}} = \frac{x_1 x_2}{S_{CC}(0)} \quad (15a)$$

where D_M is for the chemical or mutual diffusion coefficient and D_{id} is for the intrinsic diffusion coefficient for an ideal mixture and are related as

$$D_M = D_{id} \frac{\partial \ln a_A}{\partial x_1}$$

and $D_M = x_1 D_B + x_2 D_A \quad (15b)$

where D_A and D_B are the self-diffusion coefficients of pure components A and B of the liquid alloy respectively.

Surface Properties:

In this work, we have predicted the surface properties of the liquid alloys under consideration by correlating the thermodynamic properties with the modified Butler model (Bidai, Benko & Kaptay, 2005; Kaptay, 2008, 2015). According to modified Butler model, the surface tension (σ) of the liquid binary alloy of the type A–B, near the melting temperature can be given as

$$\sigma = \sigma_i^0 \frac{a_i^0}{a_i} + \frac{RT}{a_i} \ln \left(\frac{x_i^S}{x_i} \right) + \frac{\Delta G_{s,i}^E - \Delta G_i^E}{a_i} \quad (16a)$$

where σ_i^0 ($i=A, B$) represents the surface tension of the pure components, a_i^0 represents the molar surface area of components i in the pure liquid, a_i represents the molar surface area of component i in the liquid solution. $\Delta G_{s,i}^E$ stands for the surface partial excess free energy of the components, ΔG_i^E stands for the bulk partial free energy of the components, x_i represents the bulk mole fraction of the components and x_i^S represents the surface mole fraction of the components. However, the molar surface area of component in the pure liquid is equal to the molar surface area of the component in the liquid solution (i.e., $a_i^0 \approx a_i$) (Kaptay, 2008).

Under the consideration of the equilibrium between the surface and the bulk of the two components ($i=A$ and $j=B$), the Equation (16a) can be expressed as

$$\sigma = \sigma_i^0 + \frac{RT}{a_i} \ln \left(\frac{x_i^S}{x_i} \right) + \frac{\Delta G_{s,i}^E - \Delta G_i^E}{a_i} = \sigma_j^0 + \frac{RT}{a_j} \ln \left(\frac{x_j^S}{x_j} \right) + \frac{\Delta G_{s,j}^E - \Delta G_j^E}{a_j} \quad (16b)$$

where $x_i^S + x_j^S = 1$.

The molar surface area of a pure liquid metal i is computed by the relation

$$a_i = f(V_i^0)^{2/3} (N_{Av})^{1/3} \quad (17a)$$

where $N_{Av} (= 6.022 \times 10^{23} \text{ mol}^{-1})$ is the Avogadro's number, V_i^0 is the molar volume of pure metal i at the melting temperature and f is the geometrical constant.

The geometrical constant f is given as

$$f = \left(\frac{3f_b}{4} \right)^{2/3} \frac{\pi^{1/3}}{f_s} \quad (17b)$$

where f_b and f_s are the volume and surface packing fractions.

The values of f_b and f_s depends upon the type of crystal structure of the pure components of the liquid alloys.

RESULTS AND DISCUSSION

Thermodynamic Properties at Different Temperatures:

The present work has been carried out by extending regular associated solution model to predict the thermodynamic, structural and surface properties of Tl–Na liquid alloy at different temperatures. The model fit parameters, such as interaction energy parameters (ω_{12}/RT , ω_{13}/RT and ω_{23}/RT), equilibrium constant (k) and the mole fractions of the complex TlNa ($x_{Tl-Na} = x_{A,B}$) and free monomers of Tl ($x_{Tl} = x_A$) and Na ($x_{Na} = x_B$) for the Tl–Na liquid alloy at 673 K are determined from Eqs. (1), (4), (5) and (8-11) following the procedure outlined by Yadav *et al.* (2015). All the experimental data required for such procedures are taken from Hultgren *et al.* (1973). The temperature derivative terms of the interaction energy parameters ($\partial \omega_{12} / \partial T$, $\partial \omega_{13} / \partial T$ and $\partial \omega_{23} / \partial T$) required to compute and predict the thermodynamic properties of the alloy at higher temperatures are taken from Yadav *et al.* (2015). The thermodynamic properties of the concerned system

have been predicted at higher temperatures under the constraint that the mole fractions (complex as well as free monomers) and the temperature derivative terms of interaction energies remain constant for small rise in temperature of the liquid alloy above its melting temperature which is 673 K (Yadav *et al.*, 2016).

To compute and predict the thermodynamic properties of binary liquid alloys at higher temperatures, the knowledge of interaction energies at such temperatures is outmost essential. In the frame work of the preferred model, the interaction energy parameters are only temperature dependent. Eventually, they can be related with the temperature derivative terms of interaction energy parameters as follows,

$$d[\omega_{ij}(T)]_C = \frac{\partial \omega_{ij}}{\partial T} dT \quad (18a)$$

where $i, j = 1, 2$ and 3 for $i \neq j$, C is the mole fraction and $dT = T_K - T$. The term T stands for the melting temperature of the alloy which is 673 K and T_K is for the temperatures of interest which are 773 K, 873 K and 973 K.

The interaction energy parameters at higher temperatures then can be given as

$$\omega_{ij}(T_K) = \omega_{ij}(T) + \frac{\partial \omega_{ij}}{\partial T} dT \quad (18b)$$

With the help of equation (18a) and (18b) the values of interaction energy parameters as well as the temperature derivative terms of interaction energy parameters at 673 K can be determined (Yadav *et al.*, 2015). The interaction energy parameters are computed for previously mentioned temperatures and Interaction energy parameters are shown in table 1.

Table 1. Interaction energy parameters at different temperatures.

Temperature (K)	Interaction energy parameters (J mol^{-1})		
	ω_{12}	ω_{13}	ω_{23}
673	-9400.14	-12925.20	-5516.99
773	-8600.14	-11558.20	-4816.99
873	-7800.14	-10191.20	-4116.99
973	-7000.14	-8824.19	-3416.99

It can be observed from the table above that with the increase in temperature of the liquid alloy above its melting temperature, the negative values of the interaction energy parameters gradually decreases. This reveals that the strength of bonding or attraction among the constituent atoms of the alloys decreases with increase in temperature beyond 673 K.

The activity coefficients of the free monomers A and B (γ_A and γ_B ; A=Ti and B=Na) at different temperatures of interest can be computed from Equations (3a) and (3b) respectively with the aid of values from Table 1. Once the activity coefficients of unassociated atoms are determined, their activities (a_{Ti} and a_{Na}) at above stated temperatures can be estimated by using equation 2. The compositional dependence of the activities of the unassociated atoms are shown in Figure 1. It can be observed that with the increase in temperature of the concerned system above the melting temperature, the activities of the free atoms in the liquid mixture gradually increases which is in

accordance with the earlier findings (Awe *et al.*, 2011) employing different techniques. Due to the unavailability of experimental data, our findings could not be compared.

The partial excess free energy of the constituents of the liquid alloy Ti and Na then can be computed with the help of above determined activity coefficients. The expression for the partial excess free energies in terms of activity coefficients can be given as,

$$G_{A,B}^{\text{XS}} = RT \sum \ln \gamma_{A,B} \quad (19a)$$

where the terms have their usual meanings.

The excess free energy of mixing (G_M^{XS}) of the liquid alloy in terms of partial excess free energy of monomers can be related as,

$$G_M^{\text{XS}} = \sum C_{A,B} G_{A,B}^{\text{XS}} \quad (19b)$$

where C is the concentrations and $\sum C_{A,B} = 1$

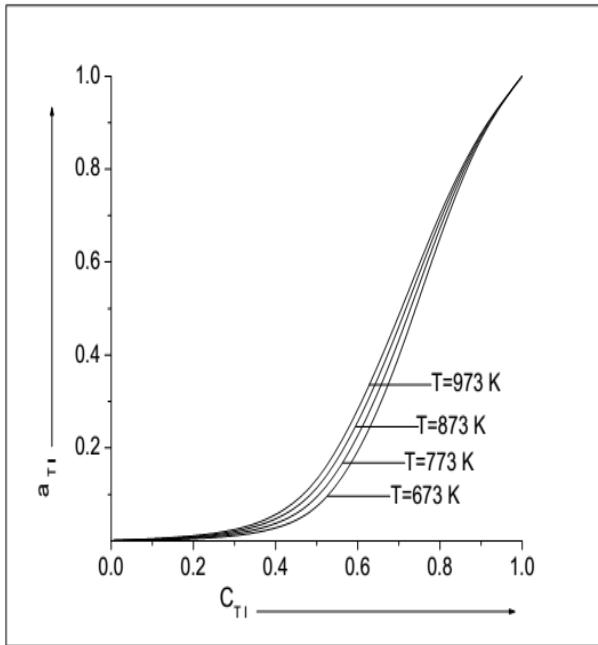


Fig. 1. (a) Activity of Tl (a_{Tl}) versus concentration of Tl (C_{Tl}) of Tl–Na liquid alloy at different temperatures.

The free energy of mixing of the concerned liquid alloy at aforementioned temperatures can be determined from the following expression

$$G_M = G_M^{XS} + RT \left(\sum C_{A,B} \ln C_{A,B} \right) \quad (19c)$$

The free energy of mixing (G_M/RT) of the liquid alloy as a function of concentration at different temperatures is shown in Fig. 2. It can be observed that at elevated temperatures, the free energy of mixing of the concerned liquid alloy decreases indicating that the strength of bonding between the constituent atoms to form the alloy decreases. It can be depicted from the perusal of Figure 2 that the values of G_M/RT at the compound forming concentration ($C_{Tl} = 0.5$) are respectively -2.1569 , -2.0745 , -1.9440 and -1.8403 at 673 K , 773 K , 873 K and 973 K . These predictions reveals that this system is the most interacting at 673 K and the strength of interacting nature decreases with increase in temperature beyond 673 K (melting temperature of the concerned alloy) and the least interacting at 973 K .

Structural Properties at different temperatures:

The concentration fluctuation in long wavelength limit ($S_{CC}(0)$) has been evolved as an important

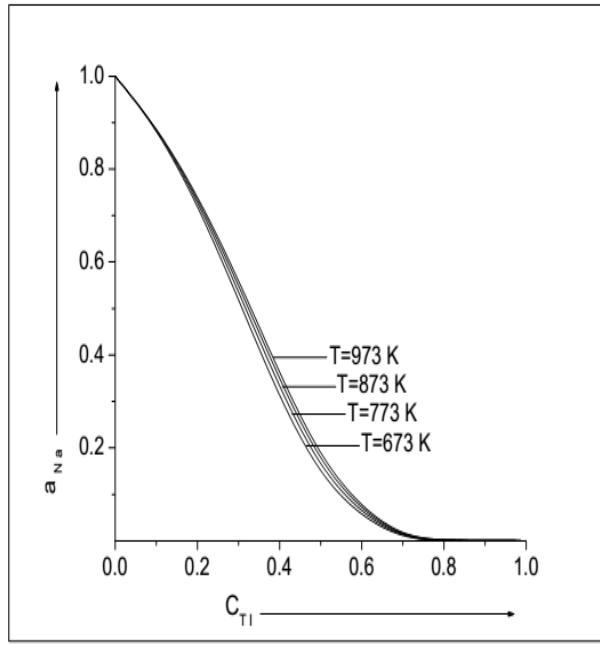


Fig. 1. (b) Activity of Na (a_{Na}) versus concentration of Tl (C_{Tl}) of Tl–Na liquid alloy at different temperatures.

parameter to understand the structural properties of binary liquid alloys, basically the mixing and demixing nature of the alloys. The mixing is generally termed as ordering where hetero-atomic association takes place and demixing is generally termed as segregating where homo-atomic association takes place in the liquid state. The theoretical values of $S_{CC}(0)$ at different temperatures can be obtained from equation 13 with the help of determined values of interaction energy parameters (Table 1).

Figure 3 shows the compositional dependence of $S_{CC}(0)$ at different temperatures. The perusal of this Figure reveals that the values of $S_{CC}(0)$ increases with increase in temperature above the melting temperature of this alloy. More precisely, the alloy shows ideal behaviour with the increase in temperature beyond its melting temperature which is relevant to the nature predicted by free energy of mixing. The theoretical investigations shows that the deviation between the ideal and computed values of $S_{CC}(0)$ at compound forming concentration ($C_{Tl} = 0.5$) are respectively 0.1964 , 0.1929 , 0.1900 and 0.1875 at 673 K , 773 K , 873 K and 973 K . Thus the concerned system is the most interacting at 673 K and the least at 973 K .

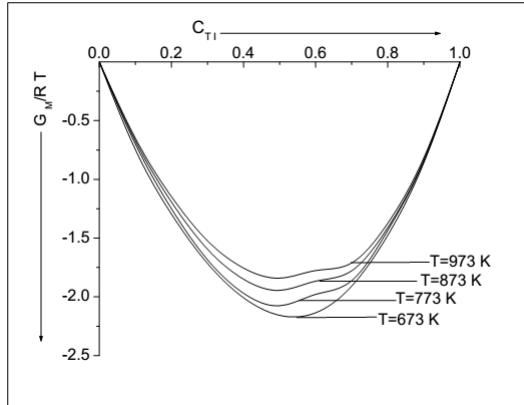


Fig. 2. Free energy of mixing (G_M/RT) versus concentration of Tl (C_{Tl}) of Tl–Na liquid alloy at different temperatures.

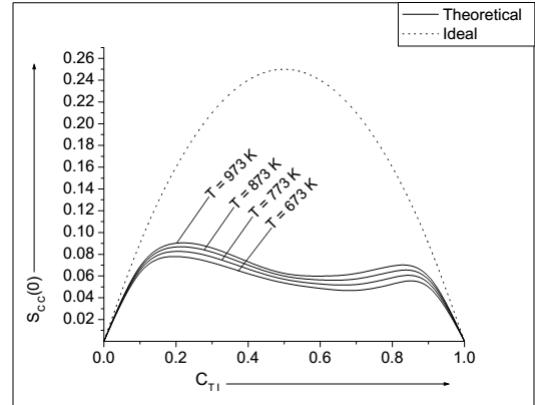


Fig. 3. Concentration fluctuation in long wavelength limit ($S_{cc}(0)$) versus concentration of Tl (C_{Tl}) of Tl–Na liquid alloy at different temperatures

To strengthen the findings about the surface properties, we have also computed the Warren-Cowley short range order parameter (α_1) using equation 14. In general, the value of α_1 lies between -1 and $+1$. The negative and positive values of α_1 respectively represent the tendency towards complex formation and segregation. Fig. 4 shows the compositional and temperature dependence of α_1 . It can be observed that the negative value of α_1 is the greatest at 673 K ($\alpha_1 = -0.2681$) and the least at 973 K ($\alpha_1 = -0.2310$) at compound forming concentration. Thus the tendency towards the complex formation of the alloy decreases with increase in its temperature beyond melting temperature which is in agreement with the nature predicted earlier.

To have greater peep into the microscopic structural behaviour we have computed and predicted the

ratio of mutual to intrinsic diffusion coefficients (D_M/D_{id}) of the preferred system. If the value of $\frac{D_M}{D_{id}} > 1$, the ordering in the liquid alloy takes place and if the value of $\frac{D_M}{D_{id}} < 1$, the segregation in the liquid alloy takes place. Theoretical value of D_M/D_{id} has been computed from equation 15 at different temperatures. The compositional and temperature dependence of D_M/D_{id} is portrayed in figure 5. The perusal of this figure shows that value of D_M/D_{id} decreases with increase in temperature of this alloy, the greatest being at 673 K ($= 4.6637$) and the least at 973 K ($= 4.0033$). Also the preferred system is found to be more interacting at 773 K where $\frac{D_M}{D_{id}} = 4.3808$ than that of 873 K where $\frac{D_M}{D_{id}} = 4.1687$.

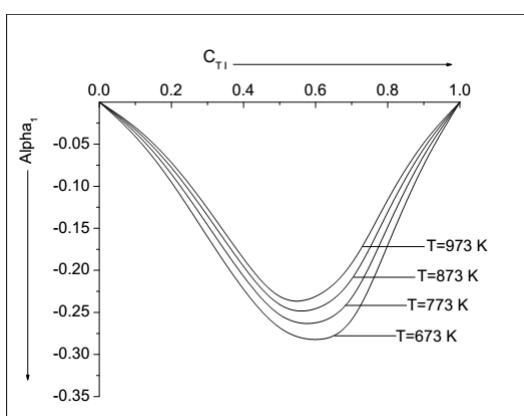


Fig. 4. Warren-Cowley short range order parameter (α_1) versus concentration of Tl (C_{Tl}) of Tl–Na liquid alloy at different temperatures.

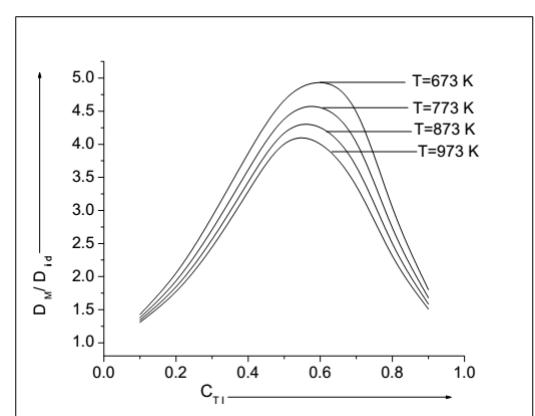


Fig. 5. Ratio of diffusion coefficients (D_M/D_{id}) versus concentration of Tl (C_{Tl}) of Tl–Na liquid alloy at different temperatures.

Surface Properties:

1. Surface Properties at T = 673 K

The surface properties of the Tl–Na liquid alloy at 673 K have been analyzed by computing surface concentrations of the free monomers and surface tension of the alloy using modified Butler model (Kaptay, 2008, 2015). The molar surface area of the constituents of the alloy ($a_i, i = A, B; A = \text{Tl} \text{ and } B = \text{Na}$) are estimated from Eq. (17) by putting $f = 1.06$ (Kaptay, 2008). The surface tension of (σ_i^0) of the pure components of the alloy at 673 K are calculated with the help of expression given below and the input parameters from Table 2.

$$\sigma_i^0 = \sigma_0 + (T - T_0) \frac{d\sigma}{dt} \quad (20)$$

where σ_0 is for the surface tension of the pure component at its melting temperature, T_0 is its melting temperature in absolute scale and $d\sigma/dt$ is temperature derivative of its surface tension.

The molar volumes of the pure components (V_i^0) are computed from the ratio of their atomic masses to densities. The densities of the component of the alloy at required temperature are then computed using the expression given below along with help of essential ingredients from table 2.

$$\rho = \rho_0 + (T - T_0) \frac{d\rho}{dt} \quad (21)$$

where ρ_0 is the density of the pure component at its melting temperature and $d\rho/dt$ is the temperature derivative of the density.

Table 2. Input parameters for surface tension (Brandes & Brook, 1992).

Metal	Melt. Temp. (K)	Density		Surface tension	
		ρ_0 (kg m ⁻³)	$\frac{d\rho}{dt}$ (kg m ⁻³ K ⁻¹)	σ_0 (mNm ⁻¹)	$\frac{d\sigma}{dt}$ (mNm ⁻¹ K ⁻¹)
Na	369.5	927	-0.2361	195	-0.0895
Tl	575	11280	-1.43	464	-0.08

The surface partial excess free energy ($\Delta G_{S,i}^E$) of the pure atom of the alloy is calculated using the relation

$$\Delta G_{S,i}^E = \beta \Delta G_i^{XS} \quad (22)$$

where ΔG_i^{XS} is the partial excess free energy whose value is taken from experimental value (Hultgren et al., 1973) at 673 K and β is the ratio of surface partial excess free energy to the bulk partial free energy of each component of the liquid mixture. The value of β is taken to be 0.8181 (Kaptay, 2015) in our calculation.

The surface tension (σ) of the liquid Tl–Na alloy at 673 K is then computed from equation 16 with the aid

of the determined values of essential input parameters as stated above. The surface concentration of the components (X_{Tl}^S and X_{Na}^S) of the alloy as a function of concentration is portrayed in figure 6. It can be observed that the surface concentration of Tl is less than the ideal value at all bulk concentration whereas the surface concentration of Na is greater than the ideal value at bulk concentration. This indicates that Tl atoms remain in bulk whereas Na atoms segregate in the surface of the liquid mixture at 673 K. Figure 7 shows the compositional dependence of surface tension of the concerned system at 673 K. It can be observed that the computed value of σ is less than the ideal values at all compositions.

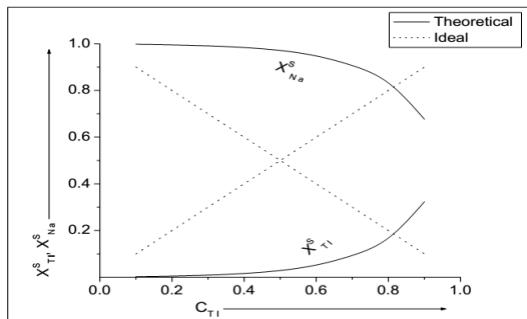


Fig. 6. Surface concentration of Tl (X_{Tl}^S) and Na (X_{Na}^S) vs concentration of Tl (C_{Tl}) of Tl–Na liquid alloy at 673 K.

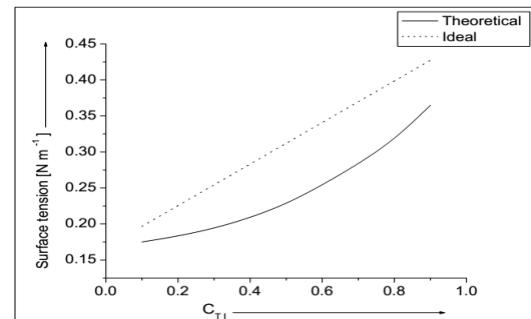


Fig. 7. Surface tension (σ) vs concentration of Tl (C_{Tl}) of Tl–Na liquid alloy at 673 K.

2. Surface Properties at Higher Temperatures ($T > 673$ K)

The surface properties of the preferred alloy at higher temperatures are computed with the help of the theoretically determined values of partial excess free energy of Tl and Na from equation 19 (a). The surface concentrations of the free monomers as well as the surface tension of the alloy at higher temperatures are determined from equation 16 employing the similar procedure as mentioned in the Section 3.3.1. The surface concentration of Tl and Na as a function of concentration at different temperature is shown in Fig. 8. The perusal of this

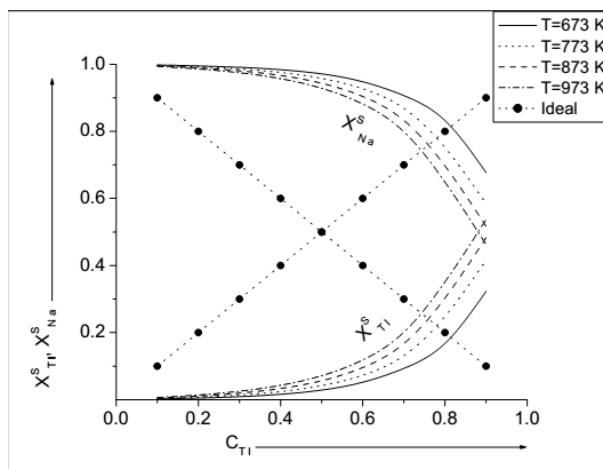


Fig. 8. Surface concentration of Tl (X_{Tl}^s) and Na (X_{Na}^s) versus concentration of Tl (C_{Tl}) of Tl–Na liquid alloy at different temperatures.

CONCLUSIONS

The modeling equations of regular associated solution have successfully predicted the thermodynamic, structural and surface properties of Tl–Na liquid alloy at different temperatures. Theoretical investigations reveal that the preferred alloy shows ideal behaviour with increase in its temperature beyond its melting temperature. Moreover, the alloy is found to be the most interacting at its melting temperature and the extent of compound forming tendency decreases at elevated temperatures.

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Figure shows that with the increase in temperature of the liquid mixture above its melting temperature, the surface concentration of Tl increases whereas that of Na decreases. This reveals that Tl atoms move towards the surface and Na atoms move towards bulk. Both of these values move towards their ideal values with increase in temperature of the liquid mixture. Figure 9 shows the compositional dependence of surface tension of the alloy at different temperatures. As expected, the surface tension of the alloy decreases with the increase in temperature of the liquid alloy.

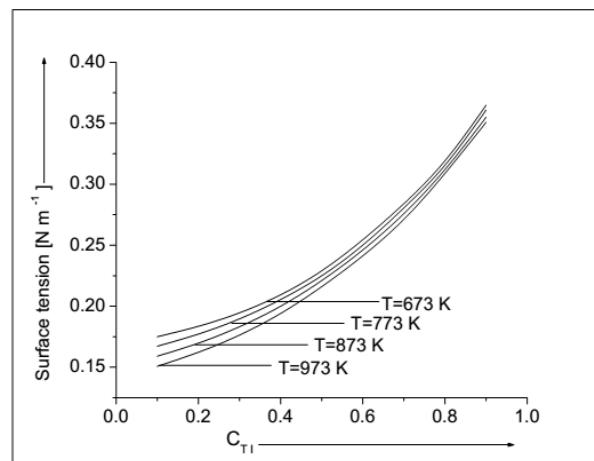


Fig. 9. Surface tension (σ) versus concentration of Tl (C_{Tl}) of Tl–Na liquid alloy at different temperatures.

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