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Thermodynamic, structural, transport and surface properties of Pb-Tl liquid alloy

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Abstract

Thermodynamic properties, such as free energy of mixing, heat of mixing, entropy of mixing, activities and the microscopic structural properties, such as concentration fluctuation in long-wavelength limit and chemical short-range order parameter of Pb-Tl liquid alloy at 773 K have been studied on the basis of regular associated solution model. We have estimated the mole fractions of the complex and the unassociated atoms assuming the existence of $PbTl_3$ complex as energetically favoured in the liquid state. The compositional contributions of the heat of mixing of the species Pb and Tl and the heat of formation of the compound to the net enthalpy change have also been studied. The transport properties such as, viscosity and the ratio of mutual and intrinsic coefficients have been studied using different approaches. The surface concentration of Tl atoms has been computed and it has been employed to calculate the surface tension of Pb-Tl liquid alloy. Both the theoretical and the experimental values of the concentration fluctuation in long-wavelength limit are found to be less than the ideal value, revealing that the concerned system is hetero-coordinating in nature. The interaction energies are found to be temperature dependent and respective alloy is found to be weakly interacting system.

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Keywords: Structural properties; compositional contributions; hetero-coordinating; transport properties, surface tension; weakly interacting.

1. Introduction

Though the direct intake thallium (Tl) is harmful to human due to its toxicity but it has wide range of uses when quenched with other atoms. It is used in the manufacture of electronic components, optical lenses, semiconductor materials, alloys, gamma radiation detector equipment, imitation jewelry, artist's paints,

low temperature thermometers and green fireworks [1-3]. It is also used as a contrast agent in the visualization of cardiac function and tumors in small amounts. Thallium forms simple eutectic alloys with tin, lead, cadmium, magnesium, etc. These alloys are resistance to wear and tear characteristics when used in bearing for steel shafts. Thallium when alloyed with lead and tin increases mechanical strain of the materials by improving the resistance against deformation, breaking strength and hardness leading to preferable uses in bearings of machine parts [4]. These multidisciplinary uses of Tl have attracted considerable attentions of the modern day researchers to predict the thermodynamic and structural properties of Tl based alloys. As the alloys are generally grown from their liquid state at temperatures near to their melting point, the properties of the initial melt have great reflection on the characteristics of alloying materials. Thus enormous work has been done by several theoreticians leading to the development of different theoretical models [5-16] for the investigations of the thermodynamic and microscopic structural behaviour of liquid binary alloys. This work is focused on the study of the thermodynamic and microscopic structural behaviour of Pb-Tl liquid alloy at 773 K on the basis of regular associated solution model [17-21].

According to the regular associated solution model, it is assumed that the liquid solution consist of an ideal mixture of free monomers and the complex in tranquility. Further there appear strong associations among the constituent species in liquid phase close to their melting points. These associations are given different names such as, 'complexes', 'pseudomolecules', 'clusters' or simply 'associations'. The initial melt thus can be considered as the ternary mixture of the associated atoms and the free monomers. The expressions for the different thermodynamic and the microscopic functions are derived on these considerations. In the microscopic structural functions, the concentration fluctuation in long wavelength limit ($S_{CC}(0)$) has become an important parameter to predict the structure of the liquid alloys. Bhatia et al, [16] has shown that the concentration fluctuation in the long wavelength limit can be obtained from the model parameters even if the data from the low angle X-ray and neutron diffraction experiments are not available. The expressions for $S_{CC}(0)$ and the thermodynamic functions of compound forming liquid binary alloys were later derived by Bhatia and Hargrove [16], however, this procedure was significantly simplified by Lele and Ramchandrarao [18] which involves the estimation of the pairwise interaction energy parameters and the equilibrium constant from the activity coefficients of the components at infinite dilution and the activity data at one another intermediate compositions. The phase diagrams of the Pb-Tl alloy [22] shows that there exhibit three different phases such as, $PbTl_2$, $PbTl_3$ and $PbTl_7$. Among these phases, we have assumed the existence of $PbTl_3$ complex and estimated its thermodynamic and structural properties. The theoretical estimation shows that there is significant asymmetry in structural properties (short range order parameters) of this alloy. The size factor and the difference in the electronegativity of the alloying materials are also the influencing parameters resulting to asymmetry. The size factors of Pb-Tl alloy ($\Omega_{Tl}/\Omega_{Pb} = 0.943$) is quite small for this behaviour. Also, the greater is the difference in the electronegativity of the alloying atoms, greater is the change in the metallic behaviour to

the ionic behaviour resulting into the asymmetry. The difference in the electronegativity of Pb-Tl liquid system ($E_{Tl} - E_{Pb} = -0.29$) is also too small for this anomalous behaviour.

The viscosity of the Pb-Tl liquid alloy at 773 K has been computed using Moelwyn-Hughes theory [23], Kozlov theory [24] and Kaptay theory [25]. The ratio of mutual to intrinsic diffusion coefficients has also been estimated to explain the nature of local arrangements of atoms in the liquid state. The surface tension of the liquid alloy has also computed using Butler's approach of mono-atomic surface layer [26].

The theory containing the methodology of this work is presented in the Section 2, the results and discussion is presented in the Section 3 and the conclusions are presented in the Section 4.

2. Theory

2.1 Thermodynamic and Structural Properties

Let the binary liquid solution consists of n_1 and n_2 atoms of the monomers A (=Tl) and B (=Pb) respectively. Then from the conservation of mass, the formation of the complex $A_\mu B$ ($A_\mu B \rightleftharpoons \mu A + B$) in the partially associated solution requires $n_1 = n_A + \mu n_{A_\mu B}$ and $n_2 = n_B + n_{A_\mu B}$, where n_A , n_B and $n_{A_\mu B}$ are respectively the concentrations of the unassociated monomers A and B and the complex $A_\mu B$ [18] and μ is a small integer whose value is determined from the complex forming concentration ($= \mu / (\mu + 1)$) in the solid state. Due to the formation of the complexes, the thermodynamic and the microscopic functions are governed by their true mole fractions x_A , x_B and $x_{A_\mu B}$ than their gross mole fractions x_1 and x_2 , where

$$x_A = \frac{n_A}{n_A + n_B + n_{A_\mu B}}, \quad x_B = \frac{n_B}{n_A + n_B + n_{A_\mu B}} \quad \text{and} \quad x_{A_\mu B} = \frac{n_{A_\mu B}}{n_A + n_B + n_{A_\mu B}} \quad (1a)$$

$$x_1 = \frac{n_1}{n_1 + n_2}, \quad x_2 = \frac{n_2}{n_1 + n_2} \quad (1b)$$

On solving above two Equations, the true mole fractions can be expressed as

$$x_A = x_1 - \mu x_2 x_{A_\mu B} \quad \text{and} \quad x_B = x_2 - (1 - \mu x_2) x_{A_\mu B} \quad (2)$$

According to Prigogine and Defay [27], in the associated solution the gross chemical potentials of the components 1 and 2 are equal to the chemical potentials of the free monomers A and B. Following Jordan [20], the activity coefficients of monomers γ_A , γ_B and $\gamma_{A_\mu B}$ can be represented in terms of pairwise interaction energies as

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

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

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

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 temperature and universal real gas constant respectively.

The relation for the equilibrium constant is expressed as [18]

$$\ln k = \ln \left(\frac{x_A^{\mu} x_B}{x_{A_{\mu}B}} \right) + \frac{\omega_{12}}{RT} + \frac{\omega_{12}}{RT} [\mu x_B (1 - x_A) + x_A] + \frac{\omega_{13}}{RT} [\mu x_{A_{\mu}B} (1 - x_A) - x_A] + \frac{\omega_{23}}{RT} [x_{A_{\mu}B} (1 - \mu x_B) - x_B] \quad (4)$$

and the free energy of mixing (G_M) is given as

$$G_M = \frac{1}{1 + \mu x_{A_{\mu}B}} RT \left[\left(x_A x_B \frac{\omega_{12}}{RT} + x_A x_{A_{\mu}B} \frac{\omega_{13}}{RT} + x_B x_{A_{\mu}B} \frac{\omega_{23}}{RT} \right) + \left(x_A \ln x_A + x_B \ln x_B + x_{A_{\mu}B} \ln x_{A_{\mu}B} \right) + x_{A_{\mu}B} \ln k \right] \quad (5)$$

The other thermodynamic functions such as heat of mixing (H_M), entropy of mixing (S_M) and the microscopic structural function, concentration fluctuation in the long wavelength limit ($S_{CC}(0)$) are correlated with free energy of mixing (G_M) by the following standard thermodynamic relations

$$H_M = G_M - T \left(\frac{\partial G_M}{\partial T} \right)_P \quad (6a)$$

$$S_M = \frac{H_M - G_M}{T} \quad (6b)$$

$$S_{CC}(0) = RT \left(\frac{\partial^2 G_M}{\partial x_1^2} \right)_{T,P}^{-1} \quad (6c)$$

$$S_{CC}(0) = x_2 \alpha_1 \left(\frac{\partial \alpha_1}{\partial x_1} \right)_{T,P}^{-1} = x_1 \alpha_2 \left(\frac{\partial \alpha_2}{\partial x_2} \right)_{T,P}^{-1} \quad (6d)$$

The expression for the enthalpy of mixing can be obtained solving Equations (5) and (6a) as

$$H_M = \frac{1}{1 + \mu x_{A_{\mu}B}} \left[\left(x_A x_B \frac{\omega_{12}}{RT} + x_A x_{A_{\mu}B} \frac{\omega_{13}}{RT} + x_B x_{A_{\mu}B} \frac{\omega_{23}}{RT} \right) - T \left(x_A x_B \frac{\partial \omega_{12}}{\partial T} + x_A x_{A_{\mu}B} \frac{\partial \omega_{13}}{\partial T} + x_B x_{A_{\mu}B} \frac{\partial \omega_{23}}{\partial T} \right) - RT^2 \frac{d \ln k}{dT} \right] \quad (7)$$

The expression for the concentration fluctuation in the long wavelength limit ($S_{CC}(0)$) can be obtained by using Equation (5) in Equations (6c) as

$$S_{CC}(0) = 1 / \left[\left(\frac{1}{1 + \mu x_{A_{\mu}B}} \right) \left\{ \frac{2}{RT} \left(x'_A x'_B w_{12} + x'_A x'_{A_{\mu}B} w_{13} + x'_B x'_{A_{\mu}B} w_{23} \right) + \left(\frac{x'^2_A}{x_A} + \frac{x'^2_B}{x_B} + \frac{x'^2_{A_{\mu}B}}{x_{A_{\mu}B}} \right) \right\} \right] \quad (8)$$

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 (2). $x'_{A_{\mu}B}$ is obtained using Equation (5) by using the condition $\frac{d \ln k}{dx_1} = 0$ [28,29]. 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 (5), (7) and (8), is a result of change in the basis for expressing mole fractions of species A, B and $A\mu B$ from that used for x_1 and x_2 .

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 (6d) using the observed values of activities [22].

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 $(S_{CC}(0))$ [16,17]. The expression for α_1 in terms of $S_{CC}(0)$ is given as

$$\alpha_1 = \frac{S-1}{S(Z-1)+1} \text{ where, } S = \frac{S_{CC}(0)}{S_{CC}^{id}(0)} \text{ and } S_{CC}^{id}(0) = x_1 x_2 \quad (9)$$

where Z is the coordination number and $Z = 10$ is taken for our calculation.

The methodology for the estimation of the equilibrium constant and the interaction energy parameters:

The unknown interaction energy parameters (ω_{12} , ω_{13} and ω_{23}), the equilibrium constant (k) and the complex concentrations can be obtained by the consideration of the activity coefficients at infinite dilution and adoption of the iterative procedure [18]. In 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.

$$\ln \gamma_1 = \ln \gamma_A + \ln \left(\frac{x_A}{x_1} \right) \quad (12a)$$

$$\text{and, } \ln \gamma_2 = \ln \gamma_B + \ln \left(\frac{x_B}{x_2} \right) \quad (12b)$$

On solving Equations (12a) and (12b), we obtain

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

$$\frac{\omega_{23}}{RT} = \frac{x_A \ln \left(\frac{\alpha_1}{x_A} \right) + (1-x_A) \ln \left(\frac{\alpha_2}{x_B} \right) - x_A (1-x_A) \frac{\omega_{12}}{RT}}{x_{A\mu B}^2} \quad (13b)$$

where α_1 and α_2 are activities of components 1 and 2 respectively.

The pairwise interaction energies, the equilibrium constants and the activity coefficients at infinite dilution can be related as [18]

$$\ln \gamma_1^0 = \frac{\omega_{12}}{RT} \quad (14a)$$

$$k \exp \left(\frac{\omega_{13}}{RT} \right) = \left(\frac{\gamma_1^0 \gamma_2^0}{\gamma_1^0 - \gamma_2^0} \right) \quad (14b)$$

On solving Equations (4), (13a) and (13b), we obtain

$$\ln k + \frac{\omega_{13}}{RT} = \left(\frac{1+x_A}{x_{A\mu B}} \right) \ln \left(\frac{\alpha_1}{x_A} \right) + \frac{x_B}{x_{A\mu B}} \left[\ln \left(\frac{\alpha_1}{x_A} \right) - \frac{\omega_{12}}{RT} \right] + \ln \left(\frac{a_1^\mu a_2}{x_{A\mu B}} \right) \quad (15)$$

After estimating the mole fraction of the complex $x_{A\mu B}$, the mole fractions of the unassociated monomers (x_A and x_B) will follow readily from Equation (2).

2.2 Transport Properties

The study of the transport properties, such as viscosity, diffusion coefficients, etc helps to understand the mixing behaviour of binary liquid alloys at the microscopic level. In this work, we have employed the following three different theoretical approaches to compute the viscosity of the Pb-Tl liquid alloy at 773 K.

The Moelwyn-Hughes equation [23] for viscosity of liquid mixture assumes that the viscous flow becomes more difficult when the cohesion energy of the alloy is increased is given as

$$\eta = (x_1\eta_1 + x_2\eta_2) \left(1 - 2x_1x_2 \cdot \frac{H_M}{RT} \right) \quad (16)$$

where η is the viscosity of the alloy, η_i ($i = 1,2$) is the viscosity of the pure components Tl and Pb respectively. The variation of viscosity, η_i with temperature T may be expressed as [30]

$$\eta_i = \eta_{0i} \exp\left(\frac{E}{RT}\right) \quad (17)$$

where η_{0i} and E are constants for pure metal, in units of viscosity and energy per mole respectively.

The Kozlov equation [24] for the viscosity of binary mixture has been derived in a theoretical way with the correlation in semi-logarithmic coordinates as

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 - \frac{H_M}{3RT} \quad (18)$$

where the symbols have the same meanings as those in Eq. (16).

The Kaptay equation [25] for the viscosity of binary mixture has been derived taking into account the theoretical relationship between the cohesion energy of the alloy and the activation energy of viscous flow assuming that in the alloys with stronger cohesion energy the viscosity will increase, and not decrease

$$\eta = \left(\frac{h N_A}{x_1 V_1 + x_2 V_2 + V^E} \right) \exp \left(\frac{x_1 G_1^* + x_2 G_2^* - (0.155 \pm 0.015) H_M}{RT} \right) \quad (19)$$

where G_i^* is the Gibb's energy of activation of the viscous flow in pure components i given by

$$G_i^* = RT \ln \left(\frac{\eta_i V_i}{h N_A} \right) \quad (20)$$

where N_A is Avogadro's number, V_i are the molar volumes of components i ($i = 1,2$), h is the Planck's constant and V^E is the excess volume upon alloy formation which can be neglected.

The greater insight of microscopic structural properties can be done by evaluating diffusion coefficient which is expressed in terms of $S_{CC}(0)$ by using Darken thermodynamic equation [31, 32] as

$$\frac{D_M}{D_{id}} = \frac{x_1 x_2}{S_{CC}(0)} \quad (21)$$

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

$$D_M = D_{id} \frac{\partial \ln a_A}{\partial x_1}, \text{ with } D_M = x_1 D_B + x_2 D_A \quad (22)$$

where, D_A and D_B are the self-diffusion coefficient of pure components A and B respectively.

2.3 Surface Properties

The surface tension of the initial melt has great influence on the formation of solid alloys by the solidification process. The metallurgical phenomenon, such as crystal growth, welding, gas absorption, nucleation of gas bubbles are minutely associated with the surface tension. The surface properties help in understanding, description and metallurgical modeling as well as prediction of structure development during solidification in the binary alloys. The Butler's method [26] has been employed to determine the surface tension of Pb-Tl alloys in liquid state at 773 K. Butler's model considers the existence of mono-atomic layer at the surface as a separate phase that is in thermodynamic equilibrium with the bulk phase. The surface tension (τ) of a binary liquid solution at temperature T in this model can be expressed as

$$\tau = \tau_1 + \frac{1}{A_1} (G_1^{E,s} - G_1^{E,b}) + \frac{RT}{A_1} (\ln x_1^s - \ln x_1) \quad (23)$$

$$\tau = \tau_2 + \frac{1}{A_2} (G_2^{E,s} - G_2^{E,b}) + \frac{RT}{A_2} (\ln x_2^s - \ln x_2) \quad (24)$$

where τ_1 and τ_2 are surface tensions, and A_1 and A_2 are the areas of the hypothetical layer at the surface of the components A and B respectively at temperature T. $G_i^{E,s}$ and $G_i^{E,b}$, ($i=1,2$), are partial excess free energies x_i and x_i^s and are mole fractions of component i in the bulk and that in the surface respectively.

The area of monatomic surface layer for the component i is obtained from the following relation

$$A_i = 1.091 N_A^{1/3} V_i^{2/3} \quad (25)$$

where N_A is Avogadro's constant and V_i represents the molar volume of the component i. The molar volume can be calculated from the atomic mass and density of the pure component at the temperature of investigation.

On solving Eqs. (23) and (24) together for the surface concentration, we can compute surface tension of a liquid alloy system if the ratio of partial excess free energy in the surface and that in the bulk is known because all other quantities are either known or can be calculated using available data for pure components. Assuming the partial excess Gibbs energy in the bulk and that in the surface to have the same concentration dependence, they can be related to each other through a parameter λ as

$$\lambda = G_i^{E,s}/G_i^{E,b} \quad (26)$$

The value of λ is considered to be 0.83 for the calculations.

3. Results and Discussion

3.1 Thermodynamic and Structural Properties

The model parameters are determined from Equation (14) with the knowledge of the observed activity coefficients [22]. The mole fraction x_{Tl-Pb} of the complex $PbTl_3$ is then estimated using Equation (15) by iterative procedure. The compositional dependence of mole fractions various species shows the maximum association of about 4.84 mole % at $x_{Tl} = 0.5$ (Figure 1).

The other model parameters are determined from Equations (4) and (13). These values are slightly adjusted by the successive approximation to explain the experimental values of the free energy of mixing [22] using Equation (5). The best fit values of so obtained are found to be

$$k = 0.623, \quad \frac{\omega_{12}}{RT} = -0.228, \quad \frac{\omega_{13}}{RT} = +2.41 \text{ and } \frac{\omega_{23}}{RT} = -1.46$$

The negative values of ω_{12}/RT and ω_{23}/RT indicates that there exists attraction between the monomers Tl and Pb, and Pb and the complex $PbTl_3$ whereas the positive value of ω_{13}/RT indicates the repulsion between the monomer Tl and the complex $PbTl_3$ in the initial melt.

The theoretical values of the free energy of mixing (G_M/RT) are calculated using Equation (5). The theoretical investigation shows that the minimum values of G_M/RT are found to be at $x_{Tl} = 0.5$ (the theoretical value of $G_M/RT = -0.79434$ and the experimental value of $G_M/RT = -0.79090$). Both the theoretical and the experimental values of G_M/RT are in well agreement (Figure 2).

The other temperature dependent model parameters are estimated using Equation (7) to explain the experimental values of the enthalpy of mixing (H_M/RT) [23]. The best fit values are found to be

$$\frac{\partial \omega_{12}}{\partial T} = +2.39 \text{ J mol}^{-1} \text{K}^{-1}, \quad \frac{\partial \omega_{13}}{\partial T} = +4.98 \text{ J mol}^{-1} \text{K}^{-1}, \quad \frac{\partial \omega_{23}}{\partial T} = +6.01 \text{ J mol}^{-1} \text{K}^{-1}$$

and $RT^2 \frac{d \ln k}{dT} = 12900 \pm 2700 \text{ J mol}^{-1}$

The theoretical values of the enthalpy of mixing (H_M/RT) are obtained from Equation (7) with the aid of above determined parameters. Both the calculated and the observed values [22] of the enthalpy have small negative values revealing the fact that the system under consideration is weakly interacting system. The minimum values H_M/RT are found to at $x_{Tl} = 0.5$ (the theoretical value of $H_M/RT = -0.18366$ and the experimental value of $H_M/RT = -0.18101$). Figure 2 shows that both the calculated and the experimental values are in well agreement.

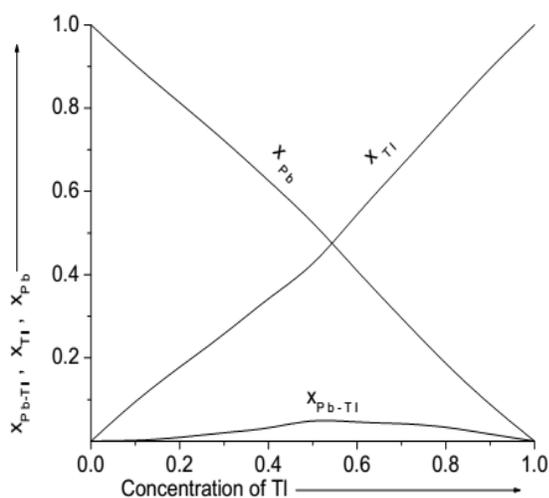


Fig. 1: Mole fractions of Pb (x_{Pb}), Tl (x_{Tl}) and $PbTl_3$ (x_{Tl-Pb}) vs concentrations of Tl (x_{Tl}) of Pb-Tl liquid alloy at 773 K.

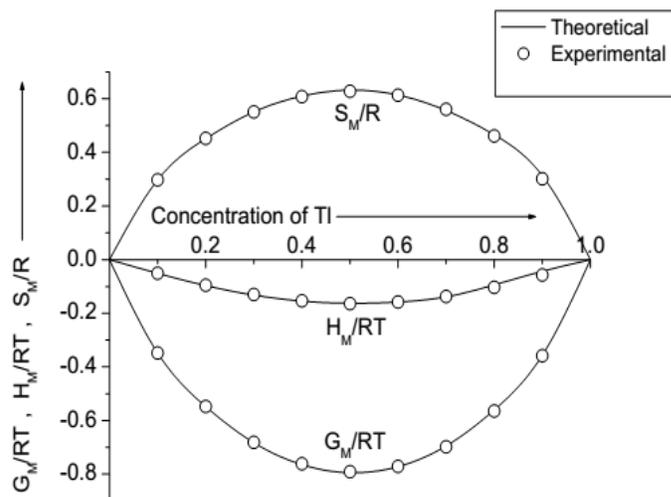


Fig. 2: Free energy of mixing (G_M/RT), heat of mixing (H_M/RT) and entropy of mixing (S_M/R) vs concentrations of Tl (x_{Tl}) of Pb-Tl liquid alloy at 773 K.

The compositional contributions of the heat of mixing of the species x_A , x_B and $x_{A\mu B}$ and the heat associated with the formation of the complexes to the net enthalpy change can be obtained from Equation (7) [33]. The complex formation term contributes the maximum at 69.49 % of Tl and the mixing term contributes the maximum at 40.68 % of Tl as a result of which the net enthalpy change shows the maximum at 50.85 % of Tl (Figure 3).

The theoretical values of the entropy of mixing (S_M/R) are obtained using Equation (6b) with the help of theoretically determined values of G_M/RT and H_M/RT . Both the experimental and the theoretical values of entropy of mixing are in well agreement (Figure 2).

The theoretical activities values for both of the unassociated species a_A and a_B ($A = Tl$ and $B = Pb$) were computed using Equations (12a) and (12b). Both the theoretical and experimental values of activities [23] are in well agreement (Figure 4). It can thus be concluded that the model parameters have not only explained the thermodynamic properties of the Pb-Tl liquid alloy at 773 K but also have successfully reproduced the activities. To peep into the microscopic behaviour of the liquid alloy, the concentration fluctuation in the long wavelength limit ($S_{CC}(0)$) was calculated. The theoretical and the experimental values are respectively obtained from Equations (8) and (6d), and the ideal values are obtained from Equation (9). Both the theoretical and the observed values of $S_{CC}(0)$ are less than the ideal value at all concentrations thereby predicting the ordering (hetero-coordinating) nature of the Pb-Tl melt at 773 K.

There is reasonable match between the theoretical and the experimental values of the concentration fluctuation in the long wavelength (Figure 5).

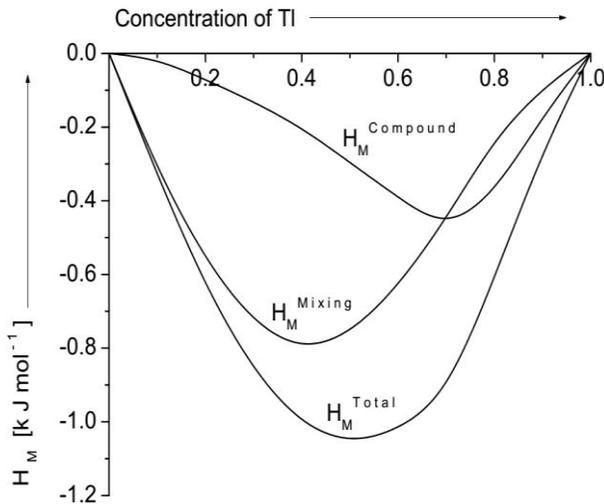


Fig. 3: Contributions of heat associated with the formation of compound and mixing of free monomers to total enthalpy change vs concentrations of Tl (x_{Tl}) of Pb-Tl liquid alloy at 773 K.

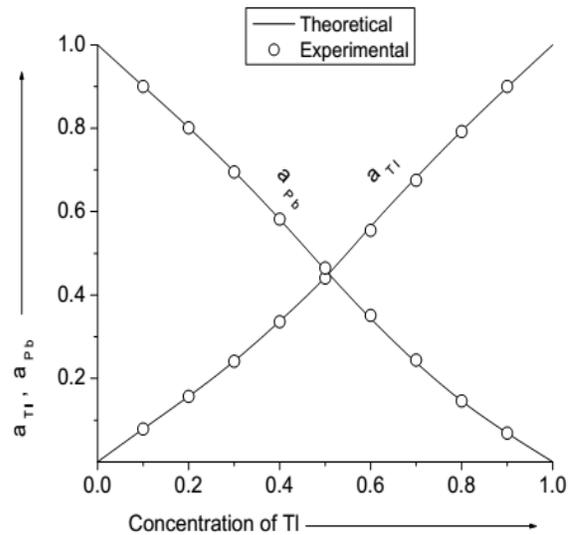


Fig. 4: The activities of Tl (a_{Tl}) and Pb (a_{Pb}) vs the concentration of Tl (x_{Tl}) of Pb-Tl liquid alloy at 773 K.

The nature and the strength of local ordering of the melt can be greater understood by estimating the short-range order parameter (α_1). At equiatomic composition, the values of α_1 lies between -1 to +1. If $\alpha_1 = -1$, indicates the complete ordering of unlike atoms at nearest neighbours, if $\alpha_1 = +1$, indicates the complete segregation or paring of like atoms in the nearest neighbours and if $\alpha_1 = 0$, indicates the complete randomness of the atoms in the liquid state. Theoretical values of α_1 are obtained from Equation (9). The compositional dependence of α_1 is shown in Figure 6. It can be seen that the values of α_1 are found to be negative at all compositions which further verifies the ordering nature of the Pb-Tl liquid alloy at 773 K.

3.2 Transport Properties

At first, the viscosities of the component metals at the temperature of investigation are computed from Eq. (17) with the aid of the values of constants η_{0i} and E which are taken from the reference [30]. The comparative study of the viscosity of the liquid alloy is then done by computing the viscosity from Eqs.

(16), (18) and (19) separately. The compositional dependence of the viscosity along with the ideal value is shown in Figure 7. With the increase in the concentration of Tl, the viscosity obtained from all the three models are greater than the ideal value but sharply decreases below the ideal value at about $x_{Tl} = 0.6$. With the further increase in the concentration of Tl, the viscosity values obtained from different model again rises above the ideal values. The values obtained from all the models are comparable with each other.

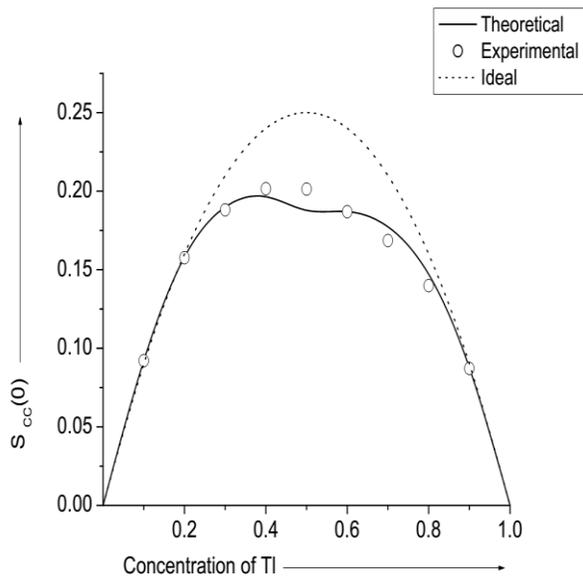


Fig. 5: The concentration fluctuation in long wavelength limit ($S_{cc}(0)$) vs the concentration of Tl (x_{Tl}) of Pb-Tl liquid alloy at 773 K.

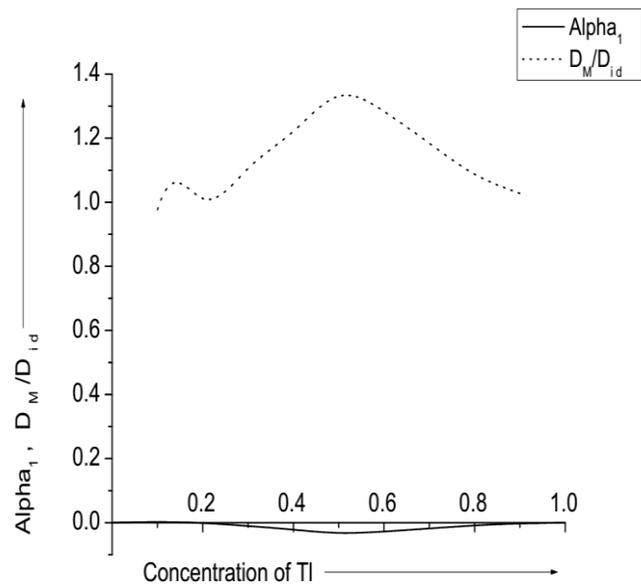


Fig. 6: The short-range ordering parameter (α_1) and the ratio of mutual and intrinsic coefficients (D_M/D_{id}) vs the concentration of Tl (x_{Tl}) of Pb-Tl liquid alloy at 773 K.

The mixing tendency of the liquid alloy can be studied at the microscopic level by computing the ratio of the mutual and intrinsic-diffusion coefficients (D_M/D_{id}). If $D_M/D_{id} > 1$, indicates the tendency of compound formation; if $D_M/D_{id} < 1$, indicates the separation of phase and $D_M/D_{id} = 1$, for the ideal mixing of the liquid alloy. The values of D_M/D_{id} are obtained from Eq. (21) and are found to be positive and greater than one in the entire compositions (Figure 6). This further clarify the theoretical analysis of the presence of the chemical order in the liquid state of Pb-Tl alloy at 773 K.

3.3 Surface Properties

The surface concentration of Tl has been computed by simultaneously solving Eqs.(23) and (24). The surface tension of the Pb-Tl liquid alloy at 773 K is then calculated using the determined values of surface

concentrations. The density and surface tension of the pure components at the temperature of investigation have been computed from the following expressions [30]

$$\rho(T) = \rho_m + \frac{\partial\rho}{\partial T}(T - T_m) \tag{26}$$

$$\tau(T) = \tau_m + \frac{\partial\tau}{\partial T}(T - T_m) \tag{27}$$

where $\frac{\partial\rho}{\partial T}$, $\frac{\partial\tau}{\partial T}$, T and T_m are temperature coefficient of density, temperature coefficient of surface tension, temperature of investigation and melting temperature respectively. The density, surface tension and temperature coefficients for pure Tl and Pb components are taken from the ref. [30].

Theoretical values of surface concentrations are almost equal to the ideal values at all concentrations (Figure 8). The value of surface tension obtained from the Butler's model is close to the ideal values (Figure 9).

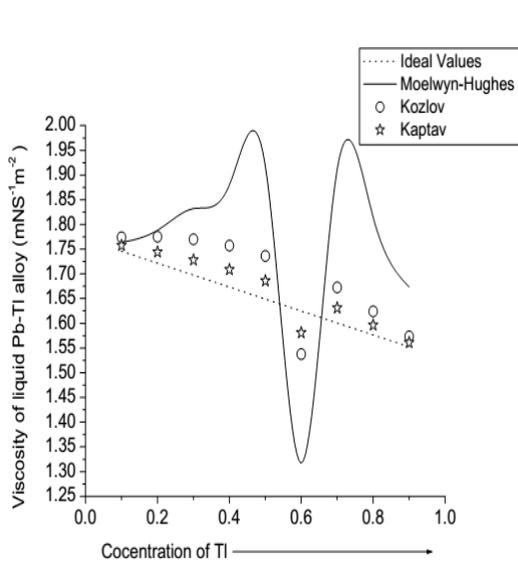


Fig. 7: Viscosity vs concentration of Tl (x_{Tl}) of Pb-Tl liquid alloy at 773 K.

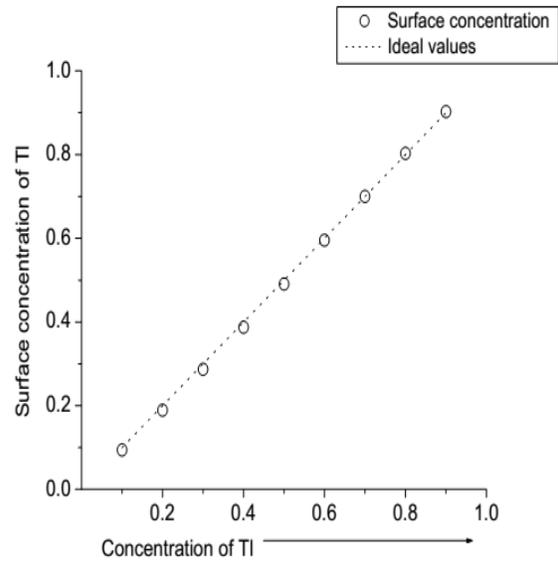


Fig. 8: Surface concentration of Tl vs concentration of Tl (x_{Tl}) of Pb-Tl liquid alloy at 773 K.

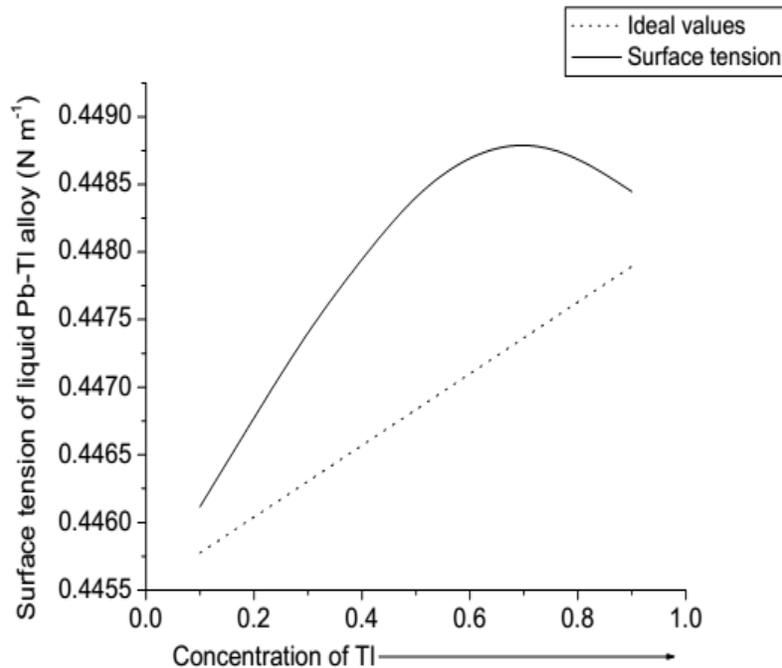


Fig. 9: Surface tension vs concentration of Tl (x_{Tl}) of Pb-Tl liquid alloy at 773K.

4. Conclusions

The regular associated solution model has been useful in understanding and predicting the thermodynamic as well as the microscopic structural properties of Pb-Tl liquid alloy at 773 K. The theoretical analysis reveals that the Pb-Tl melt is complete ordering (unlike atoms pairing) in nature. The liquid system under consideration is found to be weakly interacting and the interaction energy parameters are found to be temperature dependent.

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