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Thermophysical behavior of mercury-lead liquid alloy

N. Panthi[1,2]*, I. B. Bhandari[1], I. Koirala[1]†

Thermophysical properties of compound forming binary liquid mercury-lead alloy at temperature 600 K have been reported as a function of concentration by considering $HgPb_2$ complex using different modelling equations. The thermodynamic properties such as the Gibbs free energy, enthalpy of mixing, chemical activity of each component, and microscopic properties such as concentration fluctuation in long-wavelength limit and Warren-Cowley short range order parameter of the alloy are studied by quasi-chemical approximation. This research paper places additional emphasis on the interaction energy parameters between the atoms of the alloy. The theoretical and experimental data are compared to determine the model's validity. Compound formation model, statistical mechanical technique, and improved derivation of the Butler equation have all been used to investigate surface tension. The alloy's viscosity is investigated using the Kozlov-Ronanov-Petrov equation, the Kaptay equation, and the Budai-Benko-Kaptay model. The study depicts a weak interaction of the alloy, and the theoretical thermodynamic data derived at 600 K are in good agreement with the experimental results. The surface tension is slightly different in the compound formation model than in the statistical mechanical approach and the Butler equation at greater bulk concentrations of lead. The estimated viscosities in each of the three models are substantially identical.

I Introduction

The knowledge of thermophysical characteristics of alloys is regarded as a necessary foundation for developing novel materials. The creation of an alloy is linked to changes in the structure of a system as well as bonding between the constituent atoms. The subject is more intricately understood by studying the interaction and structural rearrangement of constituent atoms during alloy formation. The electrochemical effect, atom size, and constituent element concentration all influence the alloy's mixing properties, causing atoms of particular elements to align in either a self-coordinated or strong ordering pattern [1–4]. The alloying properties of liquid alloys vary as a function of composition, temperature, and pressure, all of which are important for the materials' strength, stability, and electrical resistivity. As a result, metallurgists and physicists have been interested in understanding the mixing behavior of metals that produce alloys. However, due to experimental difficulties as well as time limitations, the study of various alloys' characteristics is still incomplete. Different theoreticians have produced numerous concentration-dependent theoretical models to comprehend the alloying behavior of compound forming binary alloys in order to address such challenges and facilitate study as well as speed up the investigation process [5–7].

Because of their direct impact on human health, mercury and lead are the most studied metals. Our

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[*] narayan.755711@cdp.tu.edu.np
[†] iswar.koirala@cdp.tu.edu.np

[1] Central Department of Physics, Tribhuvan University, Kirtipur, Kathmandu, Nepal.

[2] Department of Physics, Patan Multiple Campus, Tribhuvan University, Nepal.

study focuses on one of the lead alloys, Hg-Pb, to theoretically determine various properties at 600 K, assuming $\mathrm{Hg}_x\mathrm{Pb}_y$ ($x = 1$, $y = 2$) complex in the melt, by using compound formation models [6]. Lead, being very soft and ductile, is often used commercially as lead alloys [8]. Zabdyr [9] explored phase diagram, crystal structure and lattice parameter by varying atomic weight percentage of Hg but the detailed thermophysical investigation is incomplete.

The properties under investigation include the Gibbs free energy of mixing, enthalpy of mixing, chemical activity, concentration fluctuation in long-wavelength limit and Warren–Cowley short-range order parameter of the alloy. Similarly, concentration-dependent surface tension and viscosity of binary liquid alloys are investigated, these being the most desirable in metallurgical research for specifying the surface and transport properties of liquid mixtures: as such, scientists are attempting to investigate these aspects by proposing several models [10–16] . Furthermore, surface segregation, which primarily refers to the concentration disparity between the alloys' surface and bulk materials, is one of the most essential elements to be investigated in metallurgical research. The difference in surface energy between the alloy's constituent elements is the fundamental source of this disparity, the element with lower surface energy tending to segregate on the surface [17]. Theoretical study indicates that the atom with a larger size tends to segregate on the surface of liquid alloy [18].

The present work also aims to study the surface tension of the alloy with a compound formation model [13]. Due to a lack of experimental data, the computed result is compared with two other models: a statistical mechanical approach [12] and an improved derivation of the Butler equation [16]. For the study of viscosity, this study employs three models; the Kozlov-Ronanov-Petrov equation [11], the Kaptay equation and the Budai-Benko-Kaptay model [10].

II Theoretical formulation

i Thermodynamic functions

Let a binary alloy contain N_A and N_B number of A and B atoms respectively. The model assumes the existence of complexes A_xB_y in such a way that

$$xA + yB = A_xB_y \tag{1}$$

where x and y are small integers.

With this assumption, the grand partition function in terms of configurational energy [6] is solved and excess free energy of mixing is obtained as given in Eq. (2) by which various properties are obtained.

$$G_M^{XS} = RT\int_0^C \gamma dC \tag{2}$$

where γ is the activity coefficient ratio of atom A to B, C is the concentration of A atom and R is universal gas constant. After simple mathematical calculation, the solution of Eq. (2) is given as

$$G_M^{XS} = N[\theta\omega + \theta_{AB}\Delta\omega_{AB} + \theta_{AA}\Delta\omega_{AA} + \theta_{BB}\Delta\omega_{BB}] \tag{3}$$

where $\theta = C(1-C)$ and $\theta_{j,k}$'s are the simple polynomials in C that depend on the values of integers x and y, ω is interchange energy, and $\Delta\omega_{jk}$ are the interaction energy parameters.

For A =Hg, B =Pb, $x = 1$, $y = 2$, the values of $\theta_{j,k}$'s are found to be [6,19]

$$\theta_{AA}(C) = 0 \tag{4}$$

$$\theta_{AB}(C) = \frac{1}{6}C + C^2 - \frac{5}{3}C^3 + \frac{1}{2}C^4 \tag{5}$$

$$\theta_{BB}(C) = -\frac{1}{4}C + \frac{1}{2}C^2 - \frac{1}{4}C^4 \tag{6}$$

The Gibbs free energy of mixing for complex formation is given by

$$\begin{aligned} G_M &= G_M^{XS} + G_M^{ideal} \\ &= G_M^{XS} + RT(C\ln C + (1-C)\ln(1-C)) \\ &= RT\left[\theta\frac{\omega}{k_BT} + \theta_{AB}\frac{\Delta\omega_{AB}}{k_BT} + \theta_{AA}\frac{\Delta\omega_{AA}}{k_BT}\right. \\ &\quad \left. + \theta_{BB}\frac{\Delta\omega_{BB}}{k_BT} + C\ln C + (1-C)\ln(1-C)\right] \end{aligned} \tag{7}$$

Here θ_{AA} is taken as zero because, according to the model used, the value of x is 1. In this case, the probability of A and A pair to be part of the complex is zero, such that the coefficient of $\frac{\Delta\omega_{AA}}{k_B T}$ in Eq. (6) also tends to zero. If there are no complexes in the alloy, then $\Delta\omega_{jk}$ is zero. In such a case, the above equation takes the form as given below:

$$G_M = RT\left[\theta\frac{\omega}{k_B T} + C\ln C + (1-C)\ln(1-C)\right] \tag{8}$$

The enthalpy of mixing is calculated with the standard thermodynamic relation:

$$\begin{aligned}\frac{H_M}{RT} &= \frac{G_M}{RT} - \left[\frac{dG_M}{RdT}\right]_{C,N,P} \\ &= \theta\left[\frac{\omega}{k_B T} - \frac{1}{k_B}\frac{d\omega}{dT}\right] \\ &\quad + \theta_{AB}\left[\frac{\Delta\omega_{AB}}{K_B T} - \frac{1}{k_B}\frac{d\Delta\omega_{AB}}{dT}\right] \\ &\quad + \theta_{BB}\left[\frac{\Delta\omega_{BB}}{K_B T} - \frac{1}{k_B}\frac{d\Delta\omega_{BB}}{dT}\right]\end{aligned} \tag{9}$$

The activity of each constituent element of the alloy is revealed following the standard thermodynamic relation,

$$RT\ln a_j(j=A,B) = G_M + (1-C)\left[\frac{\partial G_M}{\partial C_j}\right]_{T,P,N} \tag{10}$$

Now, by solving Eqs. (7) and (10), the theoretical value of activity of each constituent component is given as follows:

$$\begin{aligned}\ln a_A = \frac{G_M}{RT} + \frac{1-C}{k_B T}&\left[(1-2C)\omega + \theta'_{AB}\Delta\omega_{AB}\right. \\ &\left. + \theta'_{BB}\Delta\omega_{BB} + \ln\frac{C}{1-C}\right]\end{aligned} \tag{11}$$

$$\begin{aligned}\ln a_B = \frac{G_M}{RT} - \frac{C}{k_B T}&\left[(1-2C)\omega + \theta'_{AB}\Delta\omega_{AB}\right. \\ &\left. + \theta'_{BB}\Delta\omega_{BB} + \ln\frac{C}{1-C}\right]\end{aligned} \tag{12}$$

where, θ'_{AB}, θ'_{AA} and θ'_{BB}, respectively, are derivatives of θ_{AB}, θ_{AA} and θ_{BB} with respect to concentrations.

ii Microscopic Functions

The concentration fluctuation in the long-wavelength limit $S_{CC}(0)$for the alloy is given from the relation as [20],

$$S_{CC}(0) = RT\left[\frac{\partial^2 G_M}{\partial C^2}\right]_{T,P,N} \tag{13}$$

The value of $S_{CC}(0)$ can be obtained by using experimentally observed activities with the help of the following Eq. (14). Hence the values of $S_{CC}(0)$ obtained from this equation are called experimental values.

$$\begin{aligned}S_{CC}(0) &= a_A(1-C)\left[\frac{\partial a_A}{\partial C_A}\right]^{-1}_{T,P,N} \\ &= a_B C\left[\frac{\partial a_B}{\partial C_B}\right]^{-1}_{T,P,N}\end{aligned} \tag{14}$$

where a_A and a_B are observed activities of elements A and B respectively. For simplicity, we can write C and 1-C in place of C_A and C_B, respectively. Solving Eqs. (7) and (14), the value of $S_{CC}(0)$ is found as,

$$\begin{aligned}S_{CC}(0) = C(1-C)\Big[1 + C(1-C)\Big(&-2\frac{\omega}{K_B T} \\ &+ \theta"_{AB}\frac{\Delta\omega_{AB}}{K_B T} + \theta"_{BB}\frac{\Delta\omega_{BB}}{K_B T}\Big)\Big]^{-1}\end{aligned} \tag{15}$$

Where $\theta"_{jk}$ are second concentration derivatives of θ_{jk}.

The Warren-Cowley short-range order parameter (α_1) is related to concentration fluctuation in the long-wavelength limit [21, 22] as:

$$\alpha_1 = (S-1)[S(Z-1)+1]^{-1} \tag{16}$$

where Z is coordination number and

$$S = \frac{S_{CC}(0)}{S^{id}_{CC}(0)} \tag{17}$$

iii Transport property: viscosity

At the microscopic level, the mixing nature of molten alloy may be examined in terms of viscosity, which provides basis for some of the most fundamental theories concerning atomic transport qualities. It is regarded as one of the most important thermophysical qualities in metallurgical research, which primarily deals with industrial processes and a variety of natural occurrences. It is influenced by factors such as the liquid's composition, cohesion energy, and molar volume [23, 24]. The composition dependence of viscosity at 600 K is computed to examine the atomic transport features of the Hg-Pb alloy. But due to the lack of experimental data, viscosity is compared using three different models: the Kozlov-Ronanov-Petrov equation, the Kaptay equation, and the BBK (Budai-Benko-Kaptay) model.

a Kozlov-Ronanov-Petrov equation

In liquids, viscous flow depends on cohesive interaction, this interaction results from geometric and electronic shell effects [25]. The KRP equation has been developed to incorporate cohesion interaction in terms of enthalpic effect in order to consider the viscous flow in a liquid alloy. At temperature T, the equation is given as:

$$\ln\eta = C\ln C\ln\eta_A + (1-C)\ln\eta_B - \frac{H_M}{3RT} \tag{18}$$

where η and η_j are viscosity of the alloy and viscosity of individual elements A and B, respectively. For the metals, the variation of viscosity with temperature is given as [26]

$$\eta_j = \eta_0 \exp\frac{\epsilon}{RT} \tag{19}$$

where η_0 and ϵ are constants of each metal's units of viscosity and energy per mole.

b Kaptay equation

Kaptay developed an equation by considering the theoretical relationship between the cohesive energy and activation energy of the viscous flow. At temperature T, the equation is:

$$\begin{aligned}\eta = {} & \frac{hN_{Av}}{CV_A + (1-C)V_B + V^E} \\ & \times exp\left(\frac{CG_A + (1-C)G_B - \Phi H_M}{RT}\right)\end{aligned} \tag{20}$$

where h is Plank's constant, N_{Av} is Avogadro's number, $V_j (j = A, B)$ is the molar volume of pure metal, V^E is excess molar volume upon alloy formation, G_j is Gibb's energy of activation of the viscous flow in pure metals, and ϕ is a constant whose value is (0.155±0.015) [27]. The Gibb's energy of activation of pure metal is calculated by the following equation:

$$G_j = RT\ln\left(\frac{\eta_j V_j}{hN_{Av}}\right) \tag{21}$$

c BBK (Budai-Benko-Kaptay) model

The BBK model is used for the viscosity of multicomponent alloys. At temperature, it is given as:

$$\begin{aligned}\eta = {} & LT^{1/2}(CM_A + (1-C)M_B)^{1/2} \\ & \times (CV_A + (1-C)V_B + V^E)^{-2/3} \\ & \times exp\left[(CT_{m,A} + (1-C)T_{m,B} - \frac{H_M}{\chi R})\frac{I}{T}\right]\end{aligned} \tag{22}$$

where L and I are constants whose values are $(1.80\pm0.39)\times10^{-8} j/Kmol^{1/3})^{1/2}$ and (2.34±0.02), respectively, and χ is a semi-empirical parameter having a value equal to 25.4. Similarly M_j and T_{mJ} are, respectively, molar mass and the effective melting temperature of constituent elements of the alloy.

iv Surface property

In metallurgy and industry, the surface properties (surface tension and surface concentration) of liquid alloy or liquid metal are considered to be prime factors for the processing, as well as for the production, of new materials due to their relation with both surface and interface in the liquid metal process [28, 29]. The interfacial motion caused by the surface tension of liquid plays a major role in many industrial phenomena, hence the importance given to the surface and interfacial behaviors of liquid metals in the metallurgical process for solidification, controlling the processes of welding and casting [30].

a Compound Formation model

The model assumes that there is a compound forming tendency in the binary liquid alloy similar to that of the compound forming tendency in the solid state, in the form of short-ranged volume elements, due to the formation of intermetallic compound A_xB_y in the melt. The equation in this model is developed by using the grand partition function similar to the quasi chemical approximation. The equation at temperature T is given below:

$$\begin{aligned}
\sigma = \sigma_A &+ \frac{k_BT}{\rho}\ln\frac{C^s}{C} + \frac{\omega}{\rho}[p(f^S - f) - qf] \\
&+ \frac{\Delta\omega_{AB}}{\rho}[p(f^S_{AB} - f_{AB}) - qf_{AB}] \\
&+ \frac{\Delta\omega_{BB}}{\rho}[p(f^S_{BB} - f_{BB}) - qf_{BB}] \qquad (23) \\
= \sigma_B &+ \frac{k_BT}{\rho}\ln\frac{1-C^s}{1-C} + \frac{\omega}{\rho}[p(\varphi^S - \varphi) - q\varphi] \\
&+ \frac{\Delta\omega_{AB}}{\rho}[p(\varphi^S_{AB} - \varphi_{AB}) - q\varphi_{AB}] \\
&+ \frac{\Delta\omega_{BB}}{\rho}[p(\varphi^S_{BB} - \varphi_{BB}) - q\varphi_{BB}] \qquad (24)
\end{aligned}$$

where φ, f, φ_{jk} and f_{jk} are bulk concentration functions. Similarly, φ^S, f^S, φ^S_{jk} and f^S_{jk} are surface concentration functions, and ρ is the mean area of the surface per atom. For $x = 1$ and $y = 2$, the bulk concentration functions are [13, 31]:

$$\varphi = C^2 \qquad (25)$$

$$\begin{aligned}
\varphi_{AB} = \frac{1}{6} &+ 2(1-C) - 6(1-c)^2 + \frac{16}{3}(1-C)^3 \\
&- \frac{3}{2}(1-C)^4 \qquad (26)
\end{aligned}$$

$$\begin{aligned}
\varphi_{BB} = -\frac{1}{4} &+ (1-C) - \frac{1}{2}(1-C)^2 + (1-C)^3 \\
&- \frac{3}{4}(1-C)^4 \qquad (27)
\end{aligned}$$

$$f = (1-C)^2 \qquad (28)$$

$$f_{AB} = (1-C)^2 + \frac{10}{3}(1-C)^3 - \frac{3}{2}(1-C)^4 \qquad (29)$$

$$f_{BB} = -(1-C)^2 + \frac{3}{4}(1-C)^4 \qquad (30)$$

The functions φ^s, φ^S_{jk}, f^s and f^s_{jk} can be obtained from Eqs. (26) to (30) by replacing bulk concentration C with surface concentration C^S, while p and q are surface coordination fractions that indicate the fraction of the number of nearest neighbors of an atom within its own layer and in the adjoining layers, respectively, and and are related as $p + 2q = 1$. In a simple cubic crystal, $p = 2/3$ and $q = 1/6$. In a bcc crystal, $p = 3/5$ and $q = 1/5$, and in close packed crystal, $p = 1/2$ and $q = 1/4$. The mean atomic surface area is given by following relation [13]:

$$\rho = \sum_j C_j \rho_j \qquad (31)$$

The atomic surface area of each component is given as

$$\rho_j = 1.012\left(\frac{V_j}{N_{Av}}\right)^{2/3} \qquad (32)$$

b Statistical mechanical approach

This method is mainly based on the concept of layered structure near the interface. The model connects the surface tension to thermodynamic properties through the activity coefficient (γ_j) and the interchange energy between the components of an alloy. The equation at temperature T is given as below:

$$\sigma = \sigma_j + \frac{K_B T}{\rho} \ln \frac{C_j^S}{C_j \gamma_j} + \left[p(1 - C_j^S)^2 - q(1 - C_j)^2\right] \frac{\omega}{\rho} \qquad (33)$$

c Improved Derivation of the Butler equation

According to this model, there exists a monoatomic layer, called surface monolayer, at the surface of a liquid as a separate phase, and it is in thermodynamic equilibrium with the bulk phase. The surface tension (σ) of binary alloy at temperature T is given by the improved Butler equation as:

$$\sigma = \frac{S_j^0}{S_j} \sigma_j^0 + \frac{RT}{S_j} \ln \frac{C_j^S}{C_j^b} + \frac{G_j^{S,XS} - G_j^{b,XS}}{S_j} \qquad (34)$$

where, σ_j^0, S_j^0, S_j are surface tension of pure liquid metal, molar surface area of pure liquid metal, and partial molar surface area of j^{th} component, respectively. $G_j^{S,Xs}$ and $G_j^{b,Xs}$ are partial excess free energy of mixing in the surface and bulk of constituent elements of the alloy, respectively. The molar surface area of pure component is given as:

$$S_j^0 = \delta \left(\frac{M_j^0}{\lambda_j^0} \right)^{2/3} N_{Av}^{1/3} \qquad (35)$$

where δ, M_j^0, λ_j^0, δ and $N_A v$ are geometrical constant, molar mass, density of each constituent element at its melting temperature, and Avogadro's number, respectively. The value of geometrical constant is expressed as,

$$\delta = \left(\frac{3 f_v}{4} \right)^{2/3} \frac{\pi}{f_s} \qquad (36)$$

where f_v is volume packing fraction and f_s is surface packing fraction. For liquid metal, the values of f_v and f_s are 0.66 and 0.906 respectively [33].

III Results and discussion

i Thermodynamic and microscopic properties

Generally, the properties of binary liquid alloys depend on temperature, composition, and pressure.

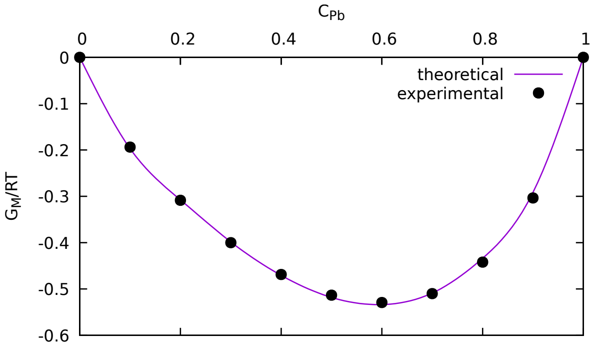

Figure 1: Gibbs free energy of mixing versus bulk concentration of Pb.

Our study of the binary alloy Hg-Pb is carried out at fixed atmospheric pressure and fixed temperature of 600 K as a function of the composition of the alloy. During the study, we assumed complexity with $x = 1$ and $y = 2$ and computed different thermodynamic and structural properties for compound forming molten alloys. The different results thus obtained from the study are outlined in the sections below.

a Thermodynamic Properties

For the analysis of the thermodynamic properties, we consider Eqs. (7), (9), (11), and (12), as mentioned above. For the Gibbs free energy of mixing, the interaction energy parameters are determined by the method of successive approximation for several concentrations, following stoichiometry of the $HgPb_2$ alloy with the help of experimental values in the concentration range (0.1 to 0.9) [34]. The approximated values of energy parameters are as follows:

$$\frac{\omega}{k_B T} = 2.139,$$
$$\frac{\Delta\omega_{AB}}{k_B T} = -2.264,$$
$$\frac{\Delta\omega_{BB}}{k_B T} = 0.392$$

To calculate the interaction energy parameters, no statistical methods such as mean square deviation were used to decide the best fit values, hence the

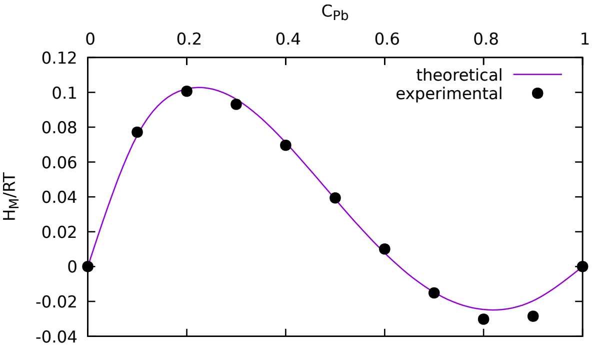

Figure 2: Enthalpy of mixing versus bulk concentration of Pb

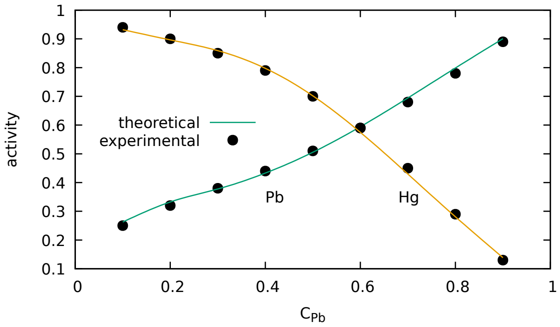

Figure 3: Chemical activity versus bulk concentration of Pb

parameters thus obtained are considered reasonable for analysis and have been considered throughout the study of different mixing properties. The computed values of G_M/RT are in good agreement with experimental values as shown in Fig. 1. The theoretically computed value of free energy of mixing is a minimum of $-0.533RT$ at 0.6 concentration of Pb. The calculation of free energy of mixing indicates that the alloy HgPb at molten state is weakly interacting. Similarly, being asymmetric at 0.5 concentration, it is classified as an irregular alloy.

The temperature derivatives of interaction energy parameters which are used for the theoretical calculation of enthalpy of mixing are obtained by the method of successive approximation. The best fit approximated values of such parameters are:

$$\begin{aligned}\frac{1}{k_B}\frac{d\omega}{dT} &= 0.767,\\ \frac{1}{k_B}\frac{d\Delta\omega_{AB}}{dT} &= -0.3128,\\ \frac{1}{k_B}\frac{d\Delta\omega_{BB}}{dT} &= 0.429\end{aligned}$$

The plot of enthalpy of mixing versus concentration of lead is shown in Fig. 2. It is positive below 0.6 concentration of lead, while above this concentration it is negative, and both computed and experimental values of enthalpy of mixing are in agreement, with small discrepancies.

The deviation of alloy from ideal behavior can be examined by chemical activity, a measure of effective concentration in the mixture, as its magnitude depends on the interaction of constituent binary components of the alloy. Equations (11) and (12) are used for the calculation of the chemical activity of elements of alloy Hg-Pb. Figure 3 plots experimental and theoretically computed values of the chemical activity of the components of the alloy, showing good agreement between the experimental and theoretical activities of the components in the alloy at temperature 600 K at all concentrations of Pb.

b Microscopic Properties

It is difficult to perform diffraction experiments on materials at high temperatures. Thus, to make the study of local arrangement of atoms in the binary alloy more effective, the concentration fluctuations in the long-wavelength limit ($S_{CC}(0)$) are

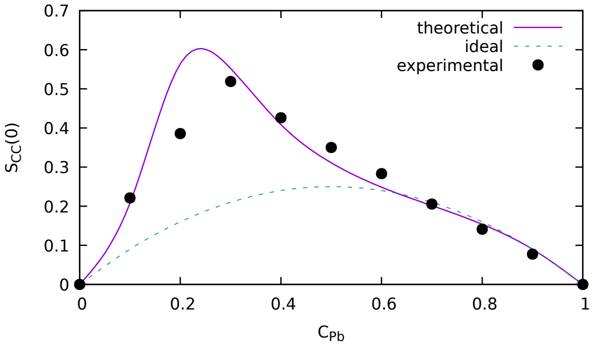

Figure 4: Concentration fluctuation in long-wavelength limit versus bulk concentration of Pb

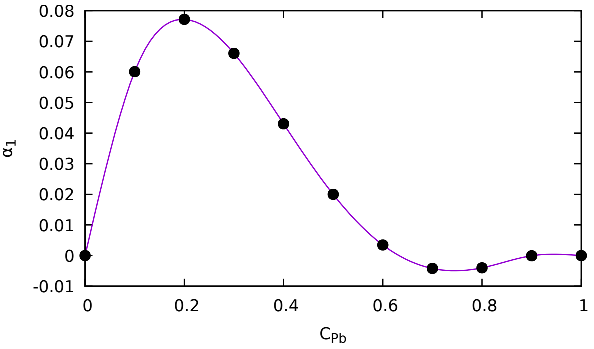

Figure 5: Warren-Cowley short-range order parameter versus bulk concentration of Pb

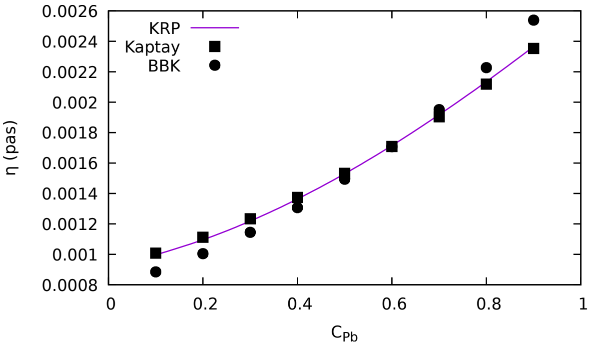

Figure 6: Viscosity versus bulk concentration of Pb

considered some of the most important microscopic functions [20, 35]. For any given concentration, if $S_{CC}(0) < S^{id}_{CC}(0)$, the alloy is expected to have complex formation in nature and if $S_{CC}(0) > S^{id}_{CC}(0)$, the expected nature of the alloy is segregating. The graph of experimental, theoretical and ideal values of $S_{CC}(0)$ versus concentration of Pb is shown in Fig. 4. In the figure, both the experimental and theoretical values of $S_{CC}(0)$ lie above the ideal value for lead concentration values below 0.6 , indicating that the alloy has a segregating nature below this concentration of lead, while above this concentration it exhibits an ordering nature.

The Warren-Cowley short range parameter (α_1) is considered one of the most powerful parameters for information regarding the arrangement of atoms in the liquid alloys. It provides quantitative information about the degree of local arrangement of atoms in the alloys. Its value lies between +1 and -1. The positive value of α_1 is considered an indication of a segregating nature, which is complete for $\alpha_1 = 1$, whereas its negative value indicates an ordering nature, and is complete for $\alpha_1 = -1$. Similarly the value $\alpha_1 = 0$ indicates the random arrangements of atoms in the liquid mixture. The value of α_1 computed as a function of the concentration of Pb using Eq. (16) is shown in Fig. 5 where we took coordination number $Z = 10$. It is observed that the α_1 is positive up to 0.6 concentration range of lead, with highest values at a concentration of 0.2, indicating the strong segregating tendency of the alloy. But above a 0.6 concentration of lead, the value of α_1 goes on decreasing, showing the ordering tendency of the alloy.

ii Viscosity

For the theoretical calculation of viscosity of Hg-Pb alloy at 600 K, the viscosities of each component (Pb and Hg) are required for KRP and Kaptay models. These values are obtained from Eq. (19) after substituting the values of η_0 and ϵ of the metals as given in reference [26]. The value of enthalpy for different concentrations is used as obtained from Eq. (9) and the Gibbs energy of activation of each pure metal is obtained from Eq. (21). Due to the lack of an experimental value for V^E, it is taken as zero. In fact, the value of V^E is non-zero for a non-ideal alloy, but the contribution of this term is very small for the determination of viscosity [15].

The results obtained from three models are compared as shown in Fig. 6. In the models, the viscosity of the liquid alloy increases with the increase in concentration of lead. The figure shows that there is a small deviation of the viscosity computed by BBK model as compared to the others. Due to the inability to compare theoretically computed results with experimental results, it becomes difficult to draw conclusions based on the models for the concentration dependence of the viscosity of Hg-Pb liquid alloy at temperature 600 K.

iii Surface segregation and surface tension

To calculate the surface tension of the alloy Hg-Pb, the densities and surface tension of individual metals for all models required at 600 K are calculated by using the relations given in reference [26].

For the compound formation model, the same interaction parameters ω and ω_{jk} used in thermody-

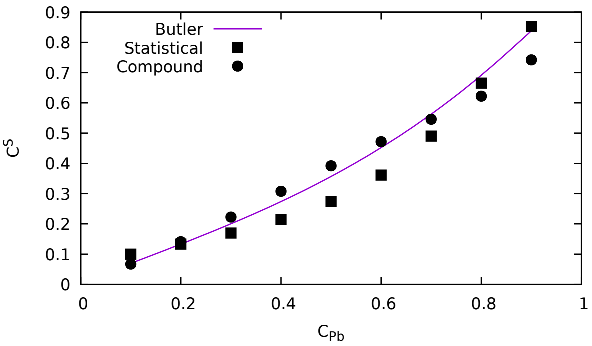

Figure 7: Surface concentration of lead versus bulk Pb concentration

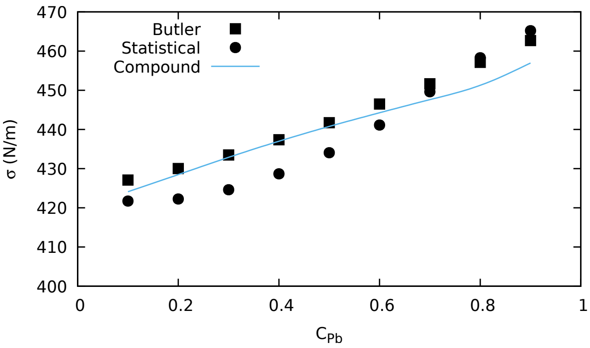

Figure 8: Surface tension versus bulk Pb concentration

namic properties are used. Now, writing these values and values of other quantities of both metals in Eqs. (23) and (24) and solving them simultaneously, we first obtain surface concentrations of both metals, and then using each surface concentration of the corresponding metals, the surface tension is obtained. A similar method is applied to the other models. For statistical mechanical approach interchange energy, $\omega = 0.699$, obtained from Eq. (8), is used.

For the improved derivation of the Butler model, the bulk and partial excess free energy of mixing of individual lead and mercury in a liquid state at 600 K are taken from reference [34]. The geometrical constant and the ratio of surface excess energy to the bulk excess energy ($G_i^{S,Xs}/G_i^{b,Xs}$) are respectively considered as 1.061 and 0.818 [33]. Kaptay suggested that, in the case of negligible or unknown excess molar volume of the mixture, the partial molar volume can be replaced by the molar volume of the same component. In such a situation, the partial surface area (S_i) is replaced by the surface area (S_i^0) of the same pure component [16,36]. The computed values of surface concentrations and surface tensions from all three models are compared in Figs. 7 and 8 respectively.

Figure 7 shows the increasing pattern of the surface concentration of Pb with the increase in bulk concentration of Lead in all models. At 600 K the surface tension of mercury is less than the surface tension of lead. This suggests the surface segregating tendency of Hg. Thus, at higher bulk concentration of Pb, two different atoms of the alloy are involved in the formation of chemical complexes or intermetallic compounds assumed to be $HgPb_2$, but at lower bulk concentration of Pb, the surface of the alloy is enriched with Hg atoms.

In Fig. 8, the surface tension of alloy Hg-Pb increases gradually with the increase in bulk concentration of Pb. The variation of surface tension in the compound formation model at higher bulk concentration of Pb than in the other two models is believed to be the cause of consideration of set of the interaction energy parameters because, as we already mentioned, there is the possibility of compound formation at higher bulk concentrations of Pb. The compound formation model is expected to give better results than the other two models due to the presence of interaction parameters. However, due to the lack of experimental results, computed results cannot be compared.

IV Conclusions

The present study is a theoretical analysis for the understanding of thermodynamic, structural, transport and surface behavior of the binary liquid alloy Hg-Pb at 600 K under the assumption of the existence of the $HgPb_2$ complex in the liquid mixture by compound formation model. The study explains the asymmetric behavior of the thermodynamic properties as a function of concentration as well as of a weakly interacting alloy. The theoretical study shows that the alloy has the nature of segregating at a lower concentration of Pb, but it shows an ordering nature at higher concentration of Pb at 600 K. Similarly, the viscosity and surface tension increases with the increase in the concentration of lead.

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