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Thermodynamic, surface, and structural properties of HgNa and HgZn liquid alloys

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ABSTRACT

We have studied the mixing behaviour and chemical ordering of Hg-Na and Hg-Zn liquid alloys by computing thermodynamic and microscopic properties at T = 673 K and T = 700 K, respectively in the framework of complex formation model. Surface properties have also been analyzed using two different approaches. The analysis suggests that the ordering energy parameters are temperature dependent and thermodynamic parameters are in good agreement with experimental results. The analysis also shows the presence of Hg_2Na complex in Hg-Na liquid alloy with a wide range of solubility than that of a weakly hetero-coordinated $HgZn_2$ complex in Hg-Zn liquid alloy. The values of surface tension obtained from two approaches for Hg-Na alloy have been found to be comparable with each other. The Hg-Zn alloy at 700 K represents a segregating system with the segregation of Zn atoms at surface.

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1. Introduction

The knowledge of thermodynamic properties, surface properties, and local atomic order are useful in metallurgical science for understanding the process of material preparation of metal alloys. Metallic alloys are technologically important due to their increased mechanical strength, heat resistance, resistance to corrosion, wear resistance and because of their economical production costs that are preferred over metals. Similarly, among the liquid alloys the knowledge of atomic transport and surface properties such as surface concentration and surface tension [1,2] are essential for the fundamental understanding of axial growth, wettability, corrosion, and all industrial processes that involve the presence of liquid phase and kinetics of phase transformation [3]. Therefore, the alloying behaviour of various liquid alloys [4–9] has been a field of continuing interest for both experimentalists [11,12] and theoreticians [7,10,13–17]. The alloying behaviour of binary liquid alloys can be studied theoretically by computing thermodynamic, transport, and surface properties. For a long time, researchers [14,17–21] have been working with several models to explain the mixing properties of liquid alloys.

The mixing properties of liquid alloys e.g. free energy of mixing, heat and entropy of mixing, and their concentration dependence are essential for detailed information about the alloying behaviour of binary liquid alloys. Microscopic functions like concentration fluctuations at long-wavelength limit and short range order parameter provide useful information about compound formation, phase separation, metallurgical processes, and material designs. Transport property such as diffusivity of metals provides insight for various chemical reactions and metallurgical processes.

In the present work, we have studied theoretically the Hg-Na and Hg-Zn alloys in molten state at temperatures T = 673 K and T = 700 K, respectively. The alloys of mercury (also known as amalgams) have applications in lighting, dentistry, and batteries [22]. Hg-Na alloy has been used as a powerful reducing agent in organic industry while the chief function of zinc in amalgam alloys is a deoxidizer. Zinc is also used in dental amalgam alloy though sparingly. The thermodynamic properties of liquid Hg-Na and Hg-Zn alloys exhibit anomalous behaviour as a function of concentration. Asymmetry in various properties of these alloys is noticed around equiatomic compositions. The size factor ($V_{Na}/V_{Hg} = 1.6$, $V_{Zn}/V_{Hg} = 0.7$) [17,23] is not large enough to account for this behaviour. However, a considerable progress has been made to explain the anomalous behaviour of thermodynamic properties of compound forming alloys with compound forming model proposed by Bhatia [20]. Later, Hoshino and Young [21] also proposed a theory for the entropy of mixing of compound forming alloys based upon hard sphere model. The theory of Hoshino opened up a new way for investigating the thermodynamic properties of liquid alloys having their tendencies to form two or more than two compounds.

In the present work, we have used compound formation model [14,24–26] with the aim to study thermodynamic properties (free energy of mixing, enthalpy and entropy of mixing) and microscopic functions (concentration fluctuations at long-wavelength limit and short

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range order) at different temperatures. At these temperatures, these alloys are liquid and metallic, whatever be the composition which is visible in their respective phase diagrams [27]. In the phase diagrams of Hg-Na and Hg-Zn alloys [22,27,28], different intermetallic compounds/complexes are indicated. Out of these, we have found that Hg_2Na complex and $HgZn_2$ are energetically favoured in Hg-Na and Hg-Zn alloys, respectively. General formalism used in these calculations is presented in the next section followed by the result and discussion part and the last section contains conclusions.

2. General formalism

2.1. Thermodynamic functions

Complex formation model [14,24–26] assumes a liquid binary alloy A–B as a ternary mixture consisting of free atoms A, free atoms B, and their preferential associations, referred as chemical complex or a compound or a pseudomolecule, $A_\alpha B_\beta$.

Let us suppose that there are n_1 atoms of A, n_2 atoms of B, and n_3 number of pseudo molecules in the alloy. We assume that only one type of chemical complex $A_\alpha B_\beta$ (α, β small integers) is formed. Therefore, the total number of scattering points are $n = n_1 + n_2 + n_3$. Here, n, n_1 and n_2 are given in terms of equilibrium values of n_3 as

$$n_1 = X_A - \alpha n_3,\ \ n_2 = 1 - X_A - \beta n_3,\ \ n = n_1 + n_2 + n_3 \ \ and \ \ n = 1 - (\alpha + \beta) n_3 \tag{1}$$

where X_A is the concentration of species A and $X_B = 1 - X_A$ is the concentration of species B. The free energy of mixing G_M of the binary alloy may be written as [26] $G_M = -n_3 g + G'$ where g is the formation energy and $-n_3 g$ represents the lowering of free energy of mixing due to the formation of compound in the alloy $A_\alpha B_\beta$ and thus the first term $-n_3 g$ represents the lowering of the free energy due to the formation of the complex in the alloy. Since strong interactions are taken care of, via the formation of chemical complexes, the mixture of atoms of species A, species B, and compound/complex $A_\alpha B_\beta$ can be treated as weakly interacting system. Hence for G', the conformal solution approximation [29] can be considered. This enables us to express G_M as [4,26]:

$$G_M = RT \sum_{i=1}^{3} n_i (ln(n_i) - ln(n)) + \sum_{i<j} \sum \frac{n_i n_j}{n} \Sigma_{ij}. \tag{2}$$

Here, $\sum_{ij} (ij = 1,2,3)$ are mutual interaction energies between the three constituents of the alloy. The equilibrium values of the chemical complex n_3 may be obtained through the condition

$$\left(\frac{\partial G_M}{\partial n_3}\right)_{T,P,C} = 0 \tag{3}$$

which gives

$$\frac{n_1^\alpha n_2^\beta}{n_3 n^{\alpha+\beta-1}} = e^{-\frac{g}{RT}} e^Y \tag{4}$$

where,

$$Y = \frac{\Sigma_{12}}{RT}\left((\alpha+\beta-1)\frac{n_1 n_2}{n^2} - \alpha\left(\frac{n_2}{n}\right) - \beta\left(\frac{n_1}{n}\right)\right) + \frac{\Sigma_{13}}{RT}\left((\alpha+\beta-1)\frac{n_1 n_3}{n^2} - \alpha\left(\frac{n_3}{n}\right) - \left(\frac{n_1}{n}\right)\right) + \frac{\Sigma_{23}}{RT}\left((\alpha+\beta-1)\frac{n_2 n_3}{n^2} - \beta\left(\frac{n_3}{n}\right) - \left(\frac{n_2}{n}\right)\right). \tag{5}$$

Eq. (4) can be solved numerically to obtain the equilibrium values of n_3.

Once the expression for G_M is obtained, other thermodynamic and microscopic functions follow readily. The enthalpy and entropy of mixing and concentration fluctuations in the long wavelength limit are related to G_M through standard thermodynamic relations. Also, in the complex formation model the evaluation of heat of mixing H_M and the entropy of mixing S_M shows the significance of temperature dependence of the energy parameters g and $\sum_{ij}$. The heat of mixing can be obtained using Eq. (2) from G_M by the relation [14]

$$H_M = G_M - T\left(\frac{\partial G_M}{\partial T}\right)_{T,P} \Rightarrow = -n_3\left(g - T\frac{\partial g}{\partial T}\right) + \sum_{i<j}\sum \frac{n_i n_j}{n}\left(\Sigma_{ij} - T\frac{\partial \Sigma_{ij}}{\partial T}\right) \tag{6}$$

and hence the entropy of mixing can be obtained as [14]

$$S_M = \frac{(H_M - G_M)}{T} \Rightarrow = n_3 \frac{\partial g}{\partial T} - R\sum_{i=1}^{3} n_i ln\frac{n_i}{n} - \sum_{i<j}\sum \frac{n_i n_j}{n}\frac{\partial \Sigma_{ij}}{\partial T}. \tag{7}$$

2.2. Structural/microscopic functions

The information about structure of liquid metal alloys can be obtained from bulk concentration fluctuations at long-wavelength limit ($Scc^b(o)$) and short range order parameter (α_1). These parameters also help to calculate the local order, degree of ordering, and level of compound activities in the alloy. $Scc^b(o)$ is obtained by differentiating Eq. (2) with respect to concentration X_A. Thus

$$S^b cc(o) = \frac{NK_B T}{\left(\frac{\partial^2 G_M}{\partial X_A^2}\right)_{T,P,N}} = \sum_{i=1}^{3} \frac{\left(n_i'\right)^2}{n_i} - \frac{\left(n'\right)^2}{n} + \frac{2n}{RT}\sum_{i<j}\sum \left(\frac{n_i}{n}\right)' \left(\frac{n_j}{n}\right)' \Sigma_{ij} \tag{8}$$

where prime denotes differentiation with respect to concentration and is given as $n_1' = 1 - \alpha n_3'$, $n_2' = -\beta n_3'$, and n_3'. In order to compare the behaviour of concentration–concentration fluctuations at the bulk and surface, concentration–concentration fluctuations on the surface [30] can also be obtained by

$$S^s cc(o) = \frac{X_A^S X_B^S}{\left[1 + (Z^S/2\varrho^S)(1-\varrho^s)\right]}.$$

Here X_A^S and X_B^S are the surface concentrations of A and B components, respectively, where $\varrho^S = [1 + 4X_A X_B(\varsigma^2 - 1)]^{1/2}$ with $\varsigma = exp(\Sigma^S/ZkT)$ and $\sum^s$ is the ordering energy on the surface [30,31] and Z^s is the coordination number of the surface atoms given by $Z^s = (x + y)Z$ and Z is the coordination number in bulk. Here x and y are surface coordination fractions.

The degree of ordering in binary alloy can be quantified by a Warren–MCowley short range order parameter α_1 [32,33]. It also measures the tendency of compound formation or phase separation in a molten alloy. It may also be defined as the probability of finding a B atom nearest to atom A. In terms of unlike atoms short range order parameter α_1 is given as

$$\alpha_1 = \frac{(S-1)}{S(Z-1)+1}, \text{where} S = \frac{S_{cc}^b(o)}{S_{cc}^{id}(o)} \tag{9}$$

here Z is the coordination number. For Hg-Na alloy, the coordination number is 10 and for Hg-Zn alloy it is 12 [34].

2.3. Diffusion

The knowledge of bulk concentration–concentration fluctuation $S_{cc}^b(o)$ can be used to investigate the nature of diffusion in liquid alloys

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