Correlation Between Thermodynamic and Surface Properties of Liquid Ag-Cu and Cd-Ga Binary Alloys

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Article Information	Abstract
	The mixing behaviour in Ag-Cu and Cd-Ga liquid alloys has been studied through the concentration dependent thermodynamic (free energy of mixing, entropy of mixing and enthalpy of mixing) as well as the microscopic functions (concentration–concentration fluctuations in long-wavelength limit and chemical short range order parameter), transport (chemical diffusion) and surface properties (surface concentration and surface tension) using the self-association model (SAM). The results obtained are in good agreement with the available experimental data on pure elements and their alloys. In addition, the results indicated that Ag-Cu and Cd-Ga alloys are segregated systems with preference for like atoms to pair as nearest neighbours in both liquid Ag-Cu and Cd-Ga alloys. The contrasting behaviours exhibited by the two liquid alloys both in the bulk and surface properties were correlated to the roles of the entropic and enthalpic effects on the mixing properties.

1. Introduction

Many studies have been documented on liquid binary alloys from both scientific and technological point of view [1-6]. Understanding the energetics of mixing when two elemental metals forms a binary alloy had long been a subject of interest to many researchers due to wide applications of alloys in modern technologies. For instance, alloys are widely used in electronics industry, photonics industry, fiber optic communication, medical implantation, aero and automobile industries, etc. Thus, the study of the thermodynamic, transport and surface properties of alloys in liquid state is very essential in elucidating the alloying behaviours of the constituents' metals as well as the corresponding properties of the resultant crystalline materials.

In this work, the concentration dependence of bulk thermodynamic, transport and surface properties of liquid Ag-Cu and Cd-Ga binary alloys have been investigated using the self-association model (SAM) developed by Singh and Sommer [4] for studying demixing/segregating liquid binary alloys. Besides high academic importance, Ag-Cu and Cd-Ga alloys have been selected for study because of their diverse commercial values and wide range of their physical and chemical properties. In addition, all the essential thermodynamic experimental data needed for the thermodynamic calculations are available at the working temperatures.

Preliminary survey of literatures reveals that thermodynamic properties of several Ag-based binary alloys such as Ag-Bi [7], Ag-Sn [8], Ag-In [9], Ag-Al [10] as well as ternary systems Ag-In-Sb [11], Ag-Sn-Zn [12] have been reported. The high interest in Ag-based alloys is not unconnected with its use as a potential lead-free solder alloys in high-temperature applications for optoelectronics such as laser diodes and photodiodes due to their good creeping properties and

high tensile strength [13]. Therefore, investigation of copper alloys with silver seems to be a logical choice.

On the other hand, cadmium is a highly reactive element which has found usage in standard electromotive cells, photovoltaic cells, fire protection system, electroplating of automotive aircraft, nuclear reactor to control the atomic fission [14]. The presence of a small quantity of cadmium in an alloy can improve the hardness, mechanical and tensile strength, fatigue strength and wear resistance. In addition, Cd–Ga may be useful in the manufacture of standard electrical materials, such as resistors, LED and quality rechargeable batteries. However, despite the observed industrial and technological significance of Ag-Cu and Cd-Ga liquid alloys, the literature data on their thermophysical properties are scarce or non-existence, while only few reference data are available for metals [15-16]. To compliment experimental efforts and provides the missing thermodynamic data, it is expected that the missing thermodynamic and thermophysical data on binary alloys will come from theoretical calculations. Different theories have been used in the study of surface properties [17-19], among which are the computer simulations [20], density functional theory [21] and the statistical mechanical theory [22-23]. In this work, the approach proposed by Prasad et al. [17, 19] was adopted. The concept has been used with lots of success within the framework of the SAM by [17, 19, 23-25].

Understanding microscopic properties such as the concentration–concentration fluctuations in long–wave length limit, $S_{cc}(0)$ and the Warren–Cowley chemical short-range order parameter (CSRO), α_1, and correlating it with both transport (Diffusion) and surface properties (Surface tension and surface concentration) of materials form the basis of studying process of formation of materials. These quantities $S_{cc}(0)$ and α_1 are capable of providing useful insight into the nature of ordering or the degree of segregation in the alloy melts. Both the compound formation tendency and phase separation behaviour in liquid alloys can be explained through these microscopic quantities in terms of hetero-coordination (preference for like atoms to pair as nearest neigbours) or homo-coordination (preference for unlike atoms to pair). For the systems studied, it is observed that both Ag-Cu and Cd-Ga liquid alloys exhibited preference for like atoms to pair as nearest neigbours i.e. two alloys are segregating in nature.

In the next section, theoretical basis for the self–association model is presented. This is followed with surface properties calculations in section 3, while results and discussion are given in section 4. Conclusion is in the last section.

2. Methodology

2.1 The self-association model (SAM)

The self-association model developed by Singh and Sommer for studying segregating liquid binary liquid alloys has been used [4]. Details of the SAM can be found in [4, 23-24]. In this model, a binary alloy consists of $N_A = Nc_A$ atoms of element A and $N_B = Nc_B$ atoms of element B, such that the total number of atoms $N = N_A + N_B$, where c_A is the concentration of A atoms in the alloy. The model assumes that the constituent atoms A and B exist in the form of a polyatomic matrix, leading to the formation of like-atom clusters or self-associates of the type A_μ and B_ν, i.e.

$$\mu A A_\mu ; \nu B \Longleftrightarrow B_\nu \tag{1}$$

where μ and ν are the number of atoms in the clusters of type A and B matrices, respectively. The thermodynamic properties of any segregating liquid alloys depends on the number of self-associates, $n = \dfrac{\mu}{\nu}$. Thus, within the framework of the model the Gibbs free energy of mixing can be expressed as:

$$\frac{G_M}{RT} = \{c_A \ln c_A + (1-c_A)\ln(1-c_A) + c_A \ln(1-\beta) + \ln\eta\} + c_A(1-c_A)\eta W \tag{2}$$

with

$$W = \mu w, \quad n = \frac{\mu}{v}, \quad \eta = \frac{1}{1-c_A\beta} \tag{3}$$

w is the ordering energy or the interchanged energy which normally gives information about the alloying behaviour in liquid binary alloys. These parameters n and w which are independent of concentration but may depend on pressure, P and temperature, T are the model parameters to be fitted at a given temperature in calculating the various bulk thermodynamic and structural properties for a given liquid binary alloy

The component activities are given as:

$$\ln a_A = \ln[c_A\eta(1-\beta)] + (1-c_A)\eta\beta + (1-c_A)^2\eta^2\frac{w}{RT} \tag{4}$$

$$\ln a_B = \ln(c_A\eta) + c_A(1-\beta)\eta(1-n) + nc_A^2(1-\beta)\eta^2\frac{w}{RT} \tag{5}$$

Once the expressions for the G_M and a_i $(i = A,B)$ are known, other thermodynamic functions readily follows.

Using standard thermodynamic relation [23-24], the entropy of mixing, S_M can be expressed as:

$$S_M = -R[c_A \ln c_A + (1-c_A)\ln(1-c_A) + c_A \ln(1-\beta) + \eta] + c_A(1-c_A)\eta\frac{\partial W}{\partial T} \tag{6}$$

and, the enthalpy of mixing, H_M, as:

$$H_M = G_M + T S_M \tag{7}$$

The concentration-concentration fluctuations at the long wavelength limits, $S_{cc}(0)$ can be obtained in terms of the free energy of mixing or in terms of activity, a_i as [4-6, 26]:

$$S_{cc}(0) = RT\left(\frac{\partial^2 G_M}{\partial c_A^2}\right)_{T,P,N}^{-1} = (1-c_A)a_A\left(\frac{\partial a_A}{\partial c_A}\right)_{T,P,N}^{-1}$$

$$= c_A a_B\left(\frac{\partial a_B}{\partial(1-c_A)}\right)_{T,P,N}^{-1} \tag{8}$$

Using Eqs. (2) and (8), an expression to calculate $S_{cc}(0)$ is written as:

$$S_{cc}(0) = \frac{c_A(1-c_A)}{1-c_A(1-c_A)g(n,w)} \tag{9}$$

Where

$$g(n,W) = \frac{2n^2\left(\frac{w}{RT}\right) - (n-1)^2[c_A + n(1-c_A)]}{[(c_A + n(1-c_A)]^3} \tag{10}$$

and for ideal mixing the energy parameter, w, in Eq. (3) is equal to zero, and Eq. (9) becomes

$$S_{cc}^{id}(0) = c_A(1 - c_A) \tag{11}$$

The Warren-Cowley chemical short-range order parameter, (α_1) is another microscopic quantity used to quantify the degree of order and segregation in the liquid alloys [2, 27-28]. This parameter α_1 can be computed theoretically using the relation:

$$\alpha_1 = \frac{P - 1}{P(Z - 1) + 1}; \quad P = \frac{S_{cc}(0)}{c(1 - c)} \tag{12}$$

Z in Eq. (12) is the coordination number whose value is taken as 10 [5, 23, 25, 29].

The relation between $S_{cc}(0)$ and the diffusion coefficients can also be employed at the microscopic level to investigate the alloying behaviour of two atomic species forming a liquid alloy due to its importance in technological and corrosion phenomena. The relation is given as [4, 23, 29]:

$$\frac{D_M}{D_{id}} = \frac{s_{cc}^{id}(0)}{S_{cc}(0)} \tag{13}$$

Where D_M is the mutual diffusion coefficient and D_{id} is the intrinsic diffusion coefficient for an ideal mixture.

2.2 Surface properties: surface concentration and surface tension

Prasad et al. [17, 19] developed an expression for the surface tension of liquid binary alloys by constructing a grand partition function for the surface in the framework of the statistical mechanical approach as:

$$\sigma = \sigma_A + \frac{k_B T}{S} \ln \frac{c_A^s}{c_A} + \frac{k_B T}{S} \ln \frac{\gamma_A^s}{\gamma_A}$$

$$= \sigma_B + \frac{k_B T}{S} \ln \frac{c_B^s}{c_B} + \frac{k_B T}{S} \ln \frac{\gamma_B^s}{\gamma_B} \tag{14}$$

Where σ_i ($i = A\ or\ B$) is the surface tension of the pure component and S is the mean atomic surface area of the alloy, computed using the relation:

$$S = \sum_i c_i S_i \quad (i = A, B) \tag{15}$$

with S_i given in terms of the atomic volumes Ω_i as

$$S_i = 1.102 \left(\frac{\Omega_i}{N_o} \right) \tag{16}$$

N_0 is Avogadro's number; c_i^s and γ_i^s refer respectively, to the concentration and activity coefficient of the ith component at the surface. γ_i and γ_i^s are related through:

$$\ln \gamma_i^s = p \left[\ln \gamma_i (c_i^s) + q \ln \gamma_i \right] \tag{17}$$

Where p and q are termed the surface coordination fractions and are defined as the fractions of the total number of nearest neighbours made by an atom within its own layer and that in the adjoining layer so that $p + 2q = 1$ with $p = 0.5$ and $q = 0.24$.

3. Results and Discussion

3.1 Thermodynamic and transport properties

The basic inputs for the computation of bulk thermodynamic properties are interaction energy parameter, w and the number of self-associates, n. The reasonable choice for w and n was made from experimental values of the free energy of mixing G_M/RT at a couple of concentrations. These values are found for Ag-Cu liquid alloys at T = 1423 K to be

$$w = 1.1200 \text{ and } n = 1.1000 \tag{18}$$

and, for Cd-Ga at 700 K to be

$$w = 1.8290 \text{ and } n = 1.0239 \tag{19}$$

The bulk thermodynamic properties of Ag-Cu and Cd-Ga liquid alloys have been computed via the expressions G_M (Eq. 3), $\ln \gamma_i$ (Eqs. 4 and 5), $S_{CC}(0)$ (Eq. 9), $S^{id}_{CC}(0)$ (Eq.11), α_1 (Eq. 12) and D_M/D_{id} (Eq. 13) as a function of concentration using the values of w and n in Eqs. (18) and (19) for Ag-Cu and Cd-Ga liquid alloys, respectively.

The calculated values of the free energy of mixing, G_M/RT for Ag-Cu and Cd-Ga liquid alloys are shown in Fig. 1. The components activities of the respective binary liquid alloys are presented in Fig. 2. It is seen from the figures that respective calculated results are in good agreement with experimental values. The experimental data were all taken from Ref. [1].

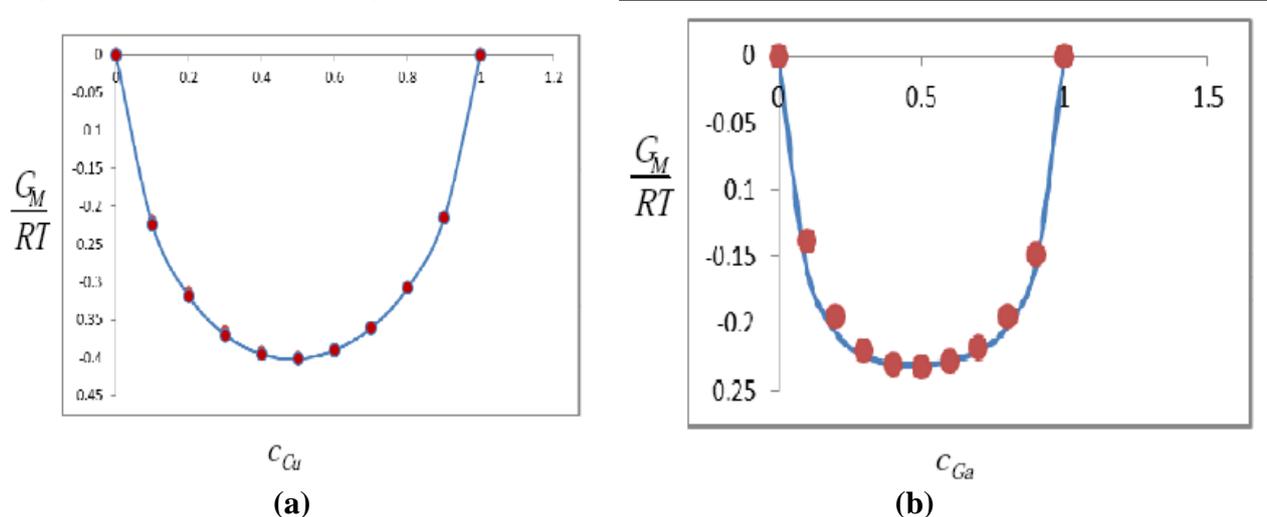(a)   (b)

Fig. 1: Free energy of mixing versus concentration (a) for Ag-Cu liquid alloy at 1423 K, (b) for Cd-Ga liquid alloy at 700 K. The solid line denotes theoretical values, while dotted circles denote experimental data. c_{Cu} and c_{Ga} are the bulk concentration of Cu and Ga in the alloy. The experimental data were taken from [1]

The plots of G_M/RT versus concentration are negative at all concentrations and symmetric around equiatomic composition. The results indicate that both alloys Ag-Cu and Cd-Ga are weakly interacting systems, with minimum G_M values of -0.4009 RT and -0.2305 RT, respectively which are less than that of strongly interacting liquid alloys like Bi-Mg ($G_M^{min} = -3.38RT$) and liquid Hg-K ($G_M^{min} = -3.35RT$) [2,25]. In addition, Fig. 1 indicates that Ag-Cu with minimum G_M values of -

0.4009 RT is more interacting than Cd-Ga liquid alloys. This implies that the tendency for like atoms (i.e. Cd-Cd or Ga-Ga) to pair as nearest neighbours is higher in Cd-Ga alloy than like atoms pairing (i.e. Ag-Ag or Cu-Cu) in Ag-Cu alloy.
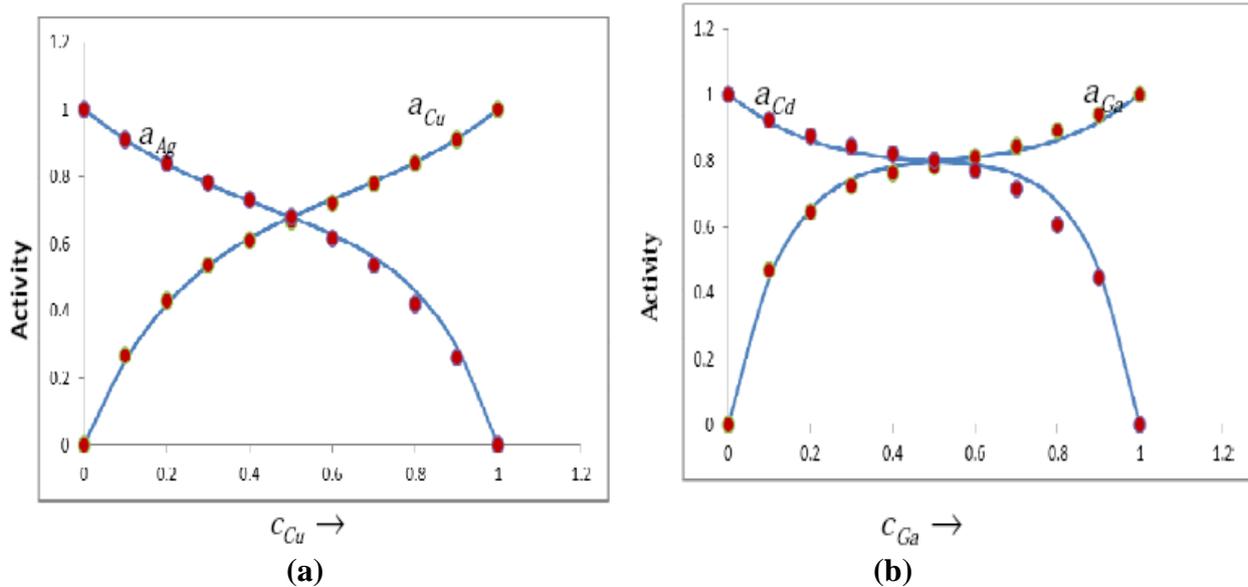

(a)   (b)

Fig. 2: Components Activities in the alloys versus concentration computed via Eqs. (4) and (5) (a) for Ag-Cu liquid alloy at 1423 K, (b) for Cd-Ga liquid alloy at 700 K. The solid line denotes theoretical values, while dotted circles denote experimental data. c_{Cu} and c_{Ga} are the bulk concentration of Cu and Ga in the alloys. The experimental data were taken from [1].

The deviation of $S_{cc}(0)$ from ideal $S_{cc}^{id}(0)$ is used to measure the nature of the alloying behaviour in a liquid binary alloy such that if calculated $S_{cc}(0) < S_{cc}^{id}(0)$, it indicates hetero-coordination of atoms i.e. preference for unlike atoms to pair as nearest neighbours). On the contrary, if calculated $S_{cc}(0) > S_{cc}^{id}(0)$ at a given concentration, then there is a tendency for homo-coordination of atoms (preference for like atoms to pair as nearest neighbours).

The computed values of $S_{cc}(0)$ are presented in Fig. 3. However, it should be noted that experimental determination of $S_{cc}(0)$ is a very difficult task due to complexities involved in carrying out experiment. The $S_{cc}(0)$ values obtained through the G_M/RT or the activity using Eq. (8) are usually taken as experimental data in the literature [3-4, 23]. These values are presented as symbols in Fig. 3 for Ag-Cu and Cd-Ga liquid alloys, respectively. It evidently seen from Fig. 3 that the calculated $S_{cc}(0) > S_{cc}^{id}(0)$ across the concentration region from 0 – 1, indicating that the two binary alloys are segregating alloys. Also, it is observed that the computed values of $S_{cc}(0)$ are in reasonable agreement with the experimental values at both temperatures.

Obviously, if ω<0, pairing of unlike atoms is preferred over pairing of like atoms. On the other hand, if ω>0, there is a tendency of like atom pairing (self-associations). 0 = ω indicates random mixing of component atoms so that the mixture is perfectly disordered [2]. We have found that ω > 0 for the Ag-Cu and Cd-Ga alloys at 1423 K and 700 K, respectively. This shows that there is a tendency to form homo-pairs in the alloys.

The values of fitted parameters w and n which gave a good representation of the experimental G_M/RT and activities of component, a_i ($i = A, B$) and $S_{cc}(0)$ in the investigated liquid alloys were then utilized to compute other thermodynamic properties of interest.
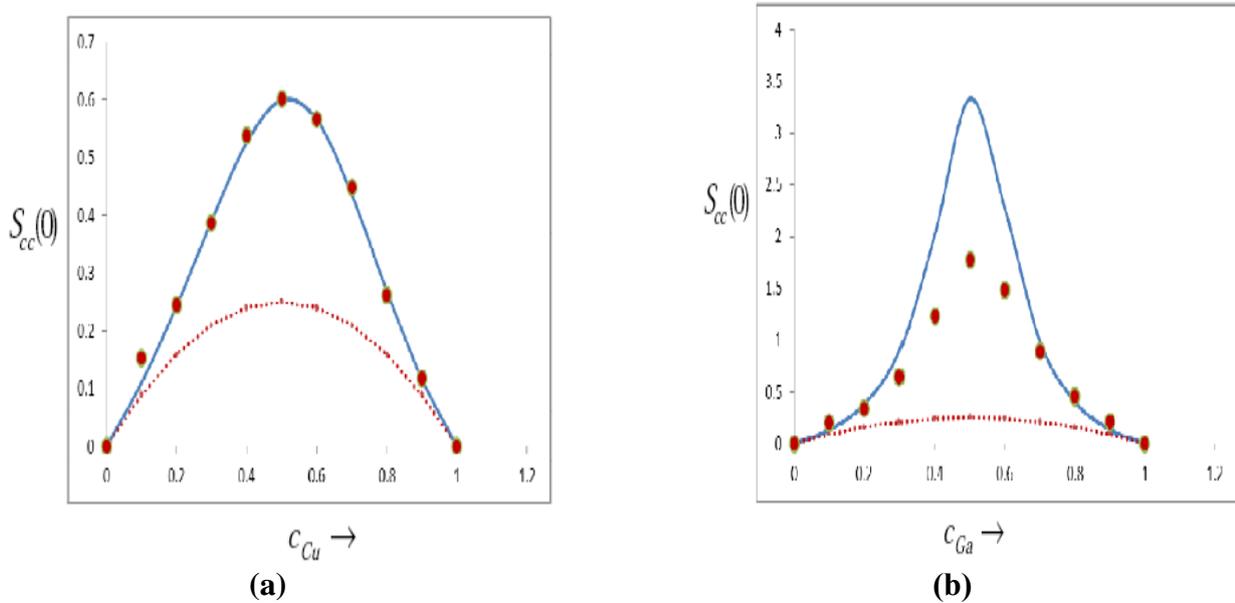

(a)　　　　　　　　　　　　　　　(b)

Fig. 3: Concentration-concentration fluctuations in the long wavelength limit, $S_{cc}(0)$ versus concentration (a) for Ag-Cu liquid alloy at 1423 K, and (b) for Cd-Ga liquid alloy at 700 K. The solid line, dotted circles and the dots denote the theoretical values, experimental data and the ideal $S_{cc}(0)$ values, respectively. c_{Cu} and c_{Ga} are the bulk concentration of Cu and Ga in the alloys. The experimental data were taken from [1].

The computed values of α_1 for the two liquid alloys are presented in Fig. 4. Our computed values of α_1 could not be compared for want of experimental values. However, from the figure it is seen that the two alloys exhibits very small positive values of α_1 at all concentration suggesting that the alloys are very weakly segregating systems.
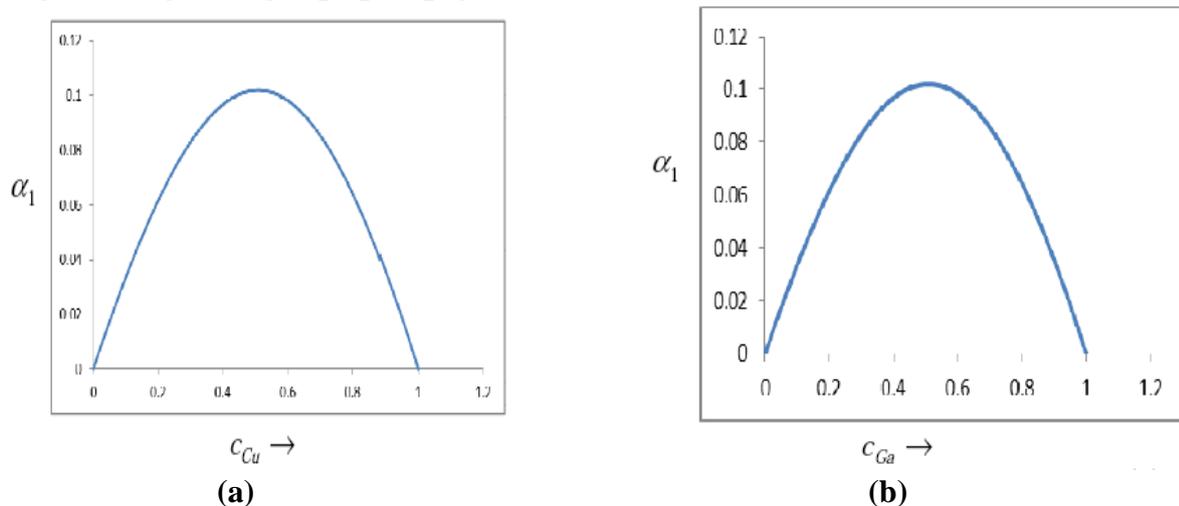

(a)　　　　　　　　　　　　　　　(b)

Fig. 4: Warren-Cowley short range order parameter, (α_1), computed using Eq. (12) versus concentration (a) for Ag-Cu liquid alloy at 1423 K, and (b) for Cd-Ga liquid alloy at 700 K. c_{Cu} and c_{Ga} are the bulk concentration of Cu and Ga in the alloys.

The computed values of $S_{cc}(0)$ have been used in Eq. (13) to assess the chemical diffusion, D_M/D_{id} as a function of concentration. These are presented in Fig 5. It is observed that the ratio $D_M/D_{id} < 1$ across the whole concentration range indicating a phase separation tendency in both Ag-Cu and Cd-Ga liquid alloys. Thus the tendency for self-coordination of atoms in the liquid alloys is energetically favoured.
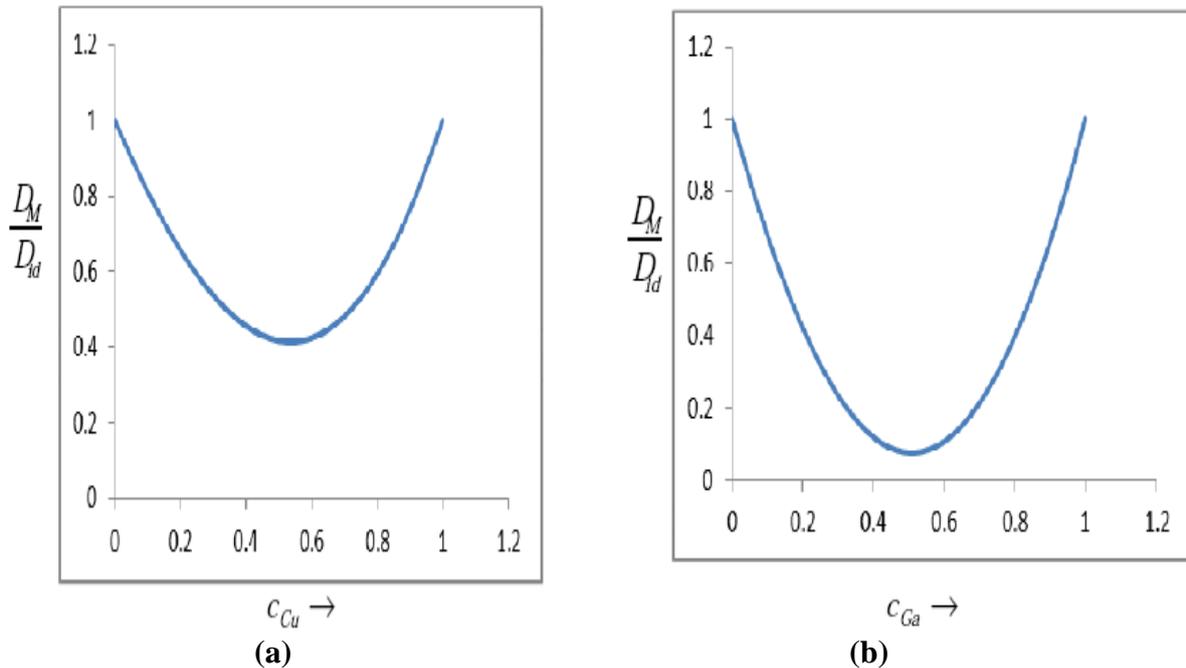

Fig. 5: Computed chemical diffusion using Eq. (13) versus concentration (a) for Ag-Cu liquid alloy at 1423 K, and (b) for Cd-Ga liquid alloy at 700 K. c_{Cu} **and** c_{Ga} **are the bulk concentration of Cu and Ga in the alloys.**

The temperature dependence of both enthalpy of mixing and the entropy of mixing was incorporated through Eqs. (6) and (7), respectively. The fitted values of dw = 0.2569 and 0.0540 for Ag-Cu and Cd-Ga alloys, respectively. One notes that both the calculated H_M/RT and S_M/R are in reasonable agreement with the experimental data except a slight deviation noticed in the H_M/RT of Cd-Ga alloys in the concentration range $0.5 < c_{Ga} < 1.0$. The values of both the H_M/RT and S_M/R are positive which is typical of segregation alloys and also symmetrical about the equiatomic concentration c = 0.5 for the alloys [4]. The plots of H_M/RT are shown in Fig. 6 while that of S_M/R are given in Fig. 7, respectively.
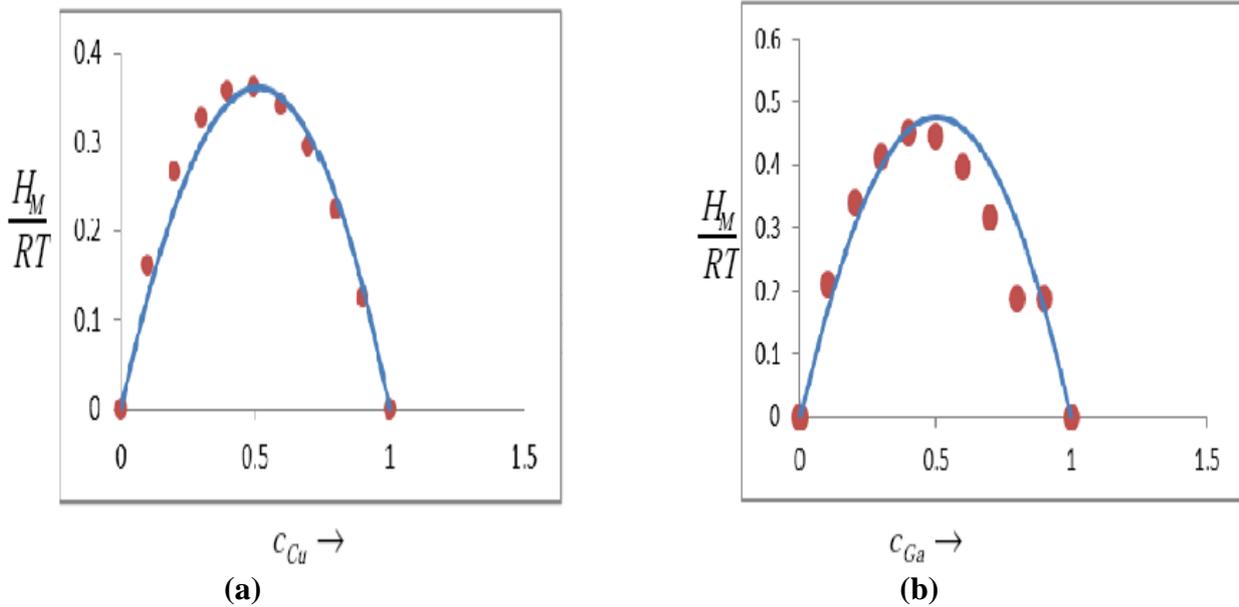
Fig. 6: Enthalpy of mixing versus concentration (a) for Ag-Cu liquid alloy at 1423 K, and (b) for Cd-Ga liquid alloy at 700 K. The solid line denotes theoretical values, while the dotted circles denote experimental data. c_{Cu} and c_{Ga} are the bulk concentration of Cu and Ga in the alloys. The experimental data were taken from [1].
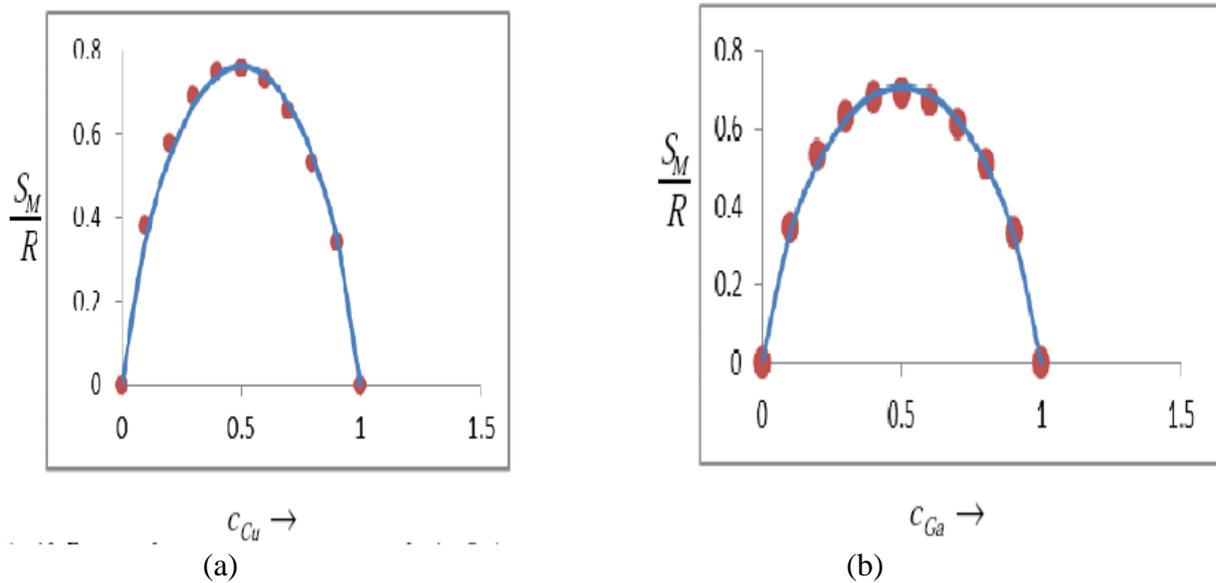

Fig. 7: Entropy of mixing versus concentration (a) for Ag-Cu liquid alloy at 1423 K, and (b) for Cd-Ga liquid alloy at 700 K. The solid line denotes theoretical values, while the dotted circles denote experimental data. c_{Cu} and c_{Ga} are the bulk concentration of Cu and Ga in the alloys. The experimental data were taken from [1].

3. 2 Surface Properties: Surface concentration and surface tension

One of the important surface properties of liquid alloys is the surface tension. It plays an important role in understanding surface-related phenomena, such as interfacial adhesion and wettability between the soldering material and the substrate from a metallurgical and catalytic point of view [17, 19, 23]. In order to produce a good wettability and strong adhesion at the substrate/solder interface, the surface tension of liquid solder must be low [30]. To calculate the surface properties at the working temperature of 1423 K for Ag –Cu and 700 K for Cd –Ga liquid alloys, the

expressions that relate the temperature dependence of surface tension with atomic volume as given in Refs [31, 32] were used to obtain the atomic volume and these are given as:

$$\sigma_i = \sigma_{im} + (T - T_m)\frac{\partial \sigma_i}{\partial T} \qquad (20)$$

and

$$\Omega_i = \Omega_{im}[1 + \theta(T - T_m)] \qquad (21)$$

where θ is the thermal coefficient of expansion, Ω_{im}, σ_{im} are the atomic volume and surface tension of the alloy components at their melting temperature T_m. T is the working temperature in Kelvin K. The values of $\frac{\partial \sigma_i}{\partial T}$ and θ for the pure component of the alloys were obtained from Ref. [31]. Equations (15) and (16) were used to compute S and Si for each atomic species of the alloy systems. The surface properties have been calculated in the framework of SAM using the same interaction energy parameters used in bulk thermodynamic calculations together with the surface tension of pure components of the individual metals listed in Table 1 as the input to estimate the values of the surface tension and surface segregation. The results obtained for the surface concentration (c_i^s) as a function of the bulk concentrations using Eq. (14) are shown in Fig. 8 for Ag – Cu and Cd- Ga alloys respectively. Fig.8a for Ag-Cu alloys, suggests that Ag-atoms segregate in the bulk for bulk concentration in the range between $0 \leq c_{Ga} \leq 0.5$ and Cu-atoms segregate to the surface for all bulk concentration in Ag-Cu liquid alloy. Similarly, the Cd-atoms are observed to segregate to the bulk for bulk concentration in the range between $0 \leq c_{Ga} \leq 0.45$ in liquid Cd-Ga alloy, whereas for bulk concentration higher than 0.45 there are more Ga-atoms in the bulk than at the surface (Fig. 8b). In the same vein, it is noted that more Cd-atoms segregate to the surface of Cd-Ga liquid alloys for bulk concentration between $0 \leq c_{Ga} \leq 0.45$ as revealed in Fig. 8b.

Table 1: Parameters used for the calculations of surface properties at different temperatures [31

Metals	T (K)	σ (N/m)	$\frac{d\sigma}{dT}$
Ag	1423	0.966	-0.190
Cu	1423	0.303	-0.230
Cd	700	0.570	-0.260
Ga	700	0.718	-0.100

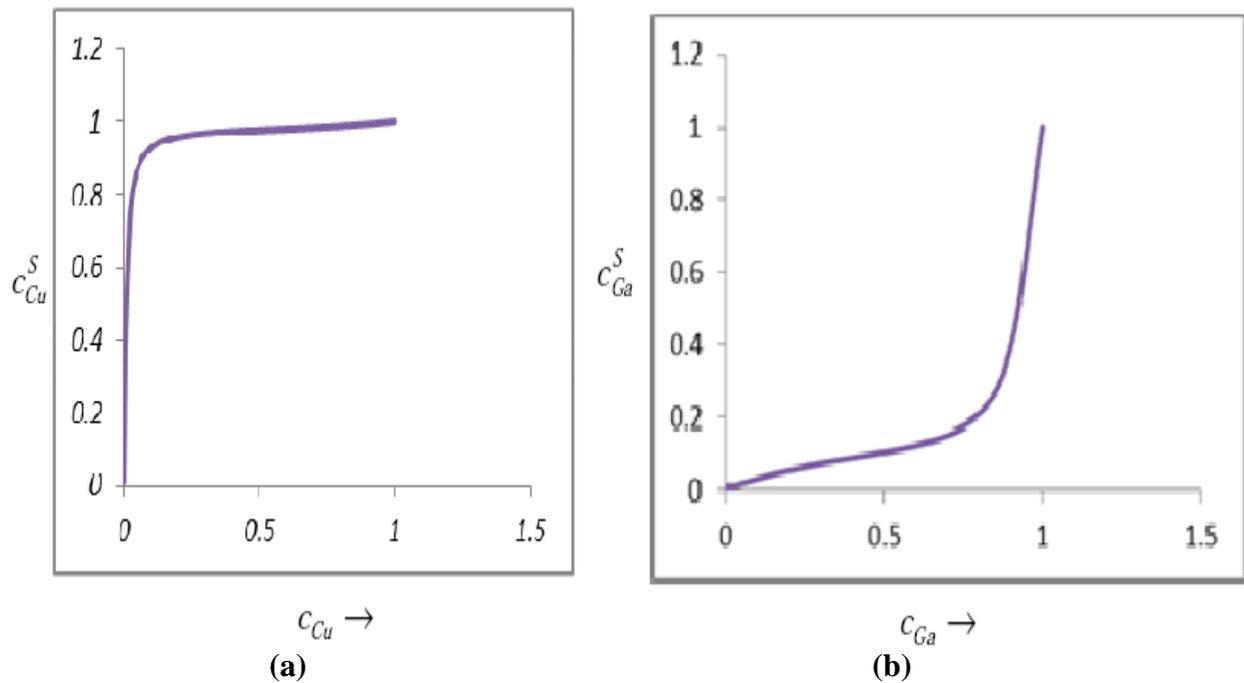(a)   (b)

Fig. 8: Computed values of the surface concentration, (c_i^s) **versus bulk concentration (a) for Ag-Cu liquid alloy at 1423 K, and (b) for Cd-Ga liquid alloy at 700 K. The curves were computed via Eq. 14. c_{Cu} and c_{Ga} are the bulk concentration of Cu and Ga in the alloys.**

Figure 8 shows that the surface concentration follows the usual trend of surface concentration increasing with increasing bulk concentration for the two alloys, it follows that the material with lower surface tension (Ag, in Ag-Cu and Cd, in Cd-Ga), segregates to the surface and, thus, minimizes the respective system's total energy. The surface tensions of the liquid alloys were calculated by inserting the surface concentration (c_i^s) values into Eq. (14). The curves describing the surface tension isothermal plots of the two liquid alloys show negative deviations from ideal mixture as seen in Fig. 9. Due to lack of surface tension experimental data our calculated surface tension isothermal curves could not be compared. The figures however indicate that Ag-atoms with lower surface tension with respect to Cu segregate to the surface of Ag-Cu alloy, while Cd-atoms also with a lower surface tension value compared to Ga segregate to the surface of Cd-Ga alloy.
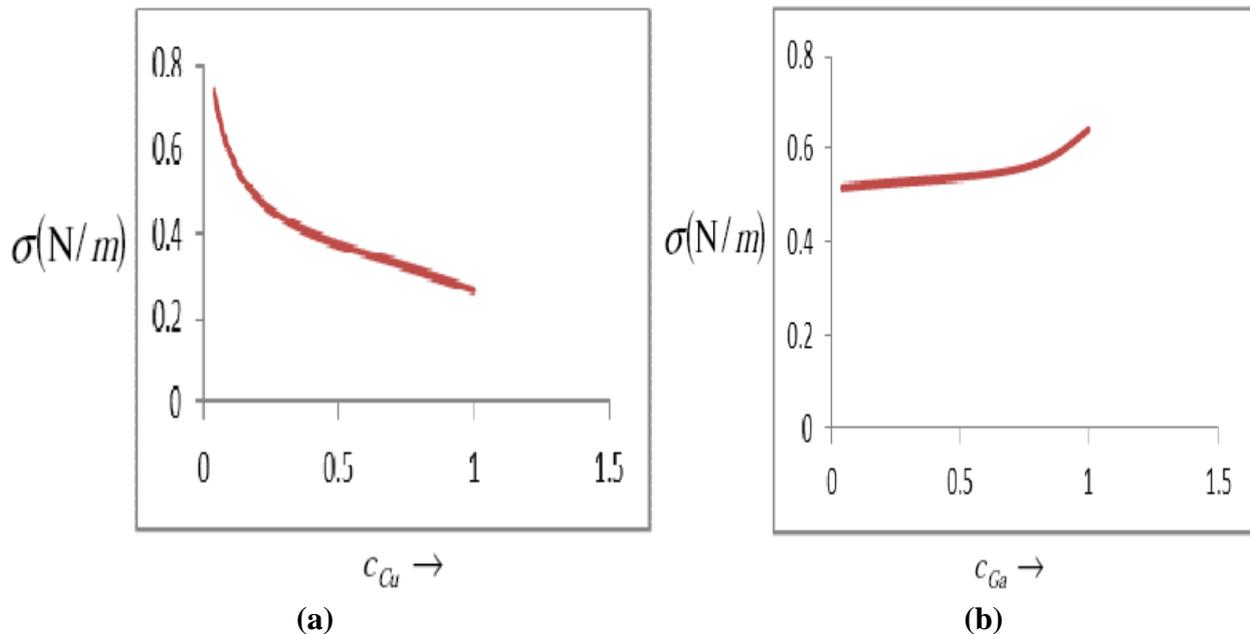
Fig. 9: Computed values of the surface tension, σ versus bulk concentration (a) for Ag-Cu liquid alloy at 1423 K, and (b) for Cd-Ga liquid alloy at 700 K. The curves were computed using Eq. (14). . c_{Cu} and c_{Ga} are the bulk concentration of Cu and Ga in the alloys.

It is observed from Fig. 9a that with the addition of Cu-atoms to Ag-Cu liquid alloy, the values of surface tension decreases as the bulk concentration (c_{Cu}) of Cu increases. In contrast, the surface tension of Cd-Ga liquid alloys increases with addition of Ga-atoms (Fig. 9b). These opposing behaviours can be explained based on the deviation of the two liquid alloys from the ideal mixture behaviour, and likewise on the difference in the surface tension of the two pure components of the alloys under investigation listed in Table 1. This behaviour, together with the results of the surface concentration indicate that even though the two alloys are segregating systems, yet, there are two opposing effects with respect to the situation in the bulk and in the surfaces. Concerning the bulk properties, it is evidently clear that the degree of segregation in Cd-Ga is higher than that in Ag-Cu, however, for the surface properties, the contrary is the case. The difference in these divergent deductions might be attributed to the roles of the enthalpic and entropic effects on the properties of mixing, since the two effects compete with one another to dictate the degree of segregation in a system [4].

4. Conclusion
The energetics of mixing in liquid Ag –Cu and Cd-Ga binary alloys has been investigated with the aim of correlating the bulk thermodynamic, transport and surface properties within the framework of the self-association model. The thermodynamic data on mixing have been used to obtain the interaction energy parameters, which are assumed to be invariant in all calculations. The results showed that Ag-Cu and Cd-Ga alloys are segregated systems with tendency of like atoms pairing in both liquid Ag-Cu and Cd-Ga alloys. The atoms with lower surface tension tend to segregate on the surface of the liquid alloys while that with higher surface tension tends to segregate inside the liquid alloys. The positive deviation in the computed surface tension from ideal mixture behaviour was reported. The divergent behaviours observed in the investigated liquid alloys both in the bulk thermodynamic and surface properties were correlated to the roles of the entropic and enthalpic effects on the alloying properties.

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