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## Correlation between bulk and surface properties in Cd–X (X = Hg, Mg) liquid alloys

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## ABSTRACT

A theoretical investigation of the energetics and its effect on the alloying behaviour of Cd–Hg and Cd–Mg liquid alloys have been carried out with the aim of correlating their bulk and surface phenomena. Using the Quasi-chemical approximation for regular solution model, our results indicate that Cd–Hg and Cd–Mg are weakly heterocoordinated both in the bulk and on the surface. We observed that the degree of chemical order in Cd–Mg liquid alloy is more than that of Cd–Hg liquid alloy.

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## 1. Introduction

A simple approach based on a statistical mechanical model, otherwise known as the first or quasi-chemical approximation (QCA) model for regular solution is used to study the bulk and the surface properties of Cd–Hg and Cd–Mg liquid alloys at temperatures of 600 K and 923 K respectively. This model has been extensively used by many authors to understand the alloying behaviour of a number of binary liquid alloys as in refs. [1–7].

QCA model is quite a suitable model for Cd–Hg and Cd–Mg since the two alloys met the following known criteria of regular alloys [8,9]:

- (i.) the size factor of their constituent atoms is negligibly small ( $\Omega_{\text{Hg}}/\Omega_{\text{Cd}} = 1.05$  and  $\Omega_{\text{Mg}}/\Omega_{\text{Cd}} = 1.09$ ,  $\Omega$  is the atomic volume at melting point).
- (ii.) the mixing properties of the two alloys are symmetric about equiatomic concentration.
- (iii.) the constituent atoms in each of the two systems have similar crystal structure (Cd and Mg have hexagonal close-packed structure while Hg has a rhombohedral structure which can be viewed as a variant of hexagonal close-packed structure [10–14]).

Essentially, the only two parameters required to successfully employ the QCA model for regular solution are the coordination number  $z$  (this is usually taken as 10) and the interchange/ordering energy  $W$  (often obtained by fitting to thermodynamic data).

The interest in the theoretical study of the energetics and its effect on the alloying behaviour of Cd–Hg and Cd–Mg liquid alloys stemmed from the understanding that:

1. despite the health hazards of Cd it has been found useful in many processes and products which include fire detection systems, pigments for plastics, ceramics and glasses, steel plating, and battery manufacturing; Cd in the form of Cadmium mercury telluride has been found useful for infra-red imaging systems in defence, space and search and rescue applications [15,16].
2. Cd like Ti, Zr and Hf is known to be highly reactive and this explains the difficulty in performing diffraction experiments on it and consequently, a structural theoretical investigation is quite desirable [1].
3. alloys of mercury (also known as amalgams) have applications in lighting, in dentistry and in batteries [14].

It is, however, necessary to mention that there have been a number of previous attempts to understand the alloying behaviours of each of these two alloys. Some of these are in refs. [1,14,17–22]. Consequently, this paper aims at complementing earlier studies on each of Cd–Hg and Cd–Mg liquid alloys, especially with the inclusion of an attempt to correlate the structural behaviours of these two Cadmium-based systems, and studies on the yet-to-be fully understood surface concentration–concentration fluctuations and surface Warren–Cowley short-range order parameter.

The essential theory behind the bulk and surface property calculations using the QCA model for regular solution is presented in the next section. This is followed by a presentation of results obtained and a discussion of the results in Sections 3 and 4 respectively. We present the concluding remarks in Section 5.

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## 2. Theory

### 2.1. Bulk properties

#### 2.1.1. Bulk Gibbs free energy of mixing, $\frac{G_M}{RT}$

In the framework of QCA model for regular solution the expression for the Gibbs free energy of mixing,  $\frac{G_M}{RT}$  is given by [1,7]

$$\frac{G_M}{RT} = c_A \ln c_A + c_B \ln c_B + c_A \ln \gamma_A + c_B \ln \gamma_B \quad (1)$$

where in Eq. (1)  $c_A$  and  $c_B$  are the bulk concentrations of components A and B in the binary alloy such that  $c_A + c_B = 1$ ,  $\gamma_A$  and  $\gamma_B$  are activity coefficients defined in the next two equations:

$$\gamma_A = \left[ \frac{(\beta - 1 + 2c_A)}{c_A(1 + \beta)} \right]^{z/2} \quad (2)$$

$$\gamma_B = \left[ \frac{(\beta + 1 - 2c_A)}{c_B(1 + \beta)} \right]^{z/2} \quad (3)$$

where in Eqs. (2) and (3)  $\beta$  is defined as [1]

$$\beta = \sqrt{(1 + 4c_A c_B [\exp(2W/zk_B T) - 1])} \quad (4)$$

In Eq. (4)  $z$  is the coordination number whose value is usually taken as 10 as explained in ref [23] while the parameter  $W$  is the ordering energy of the alloy whose value gives information on the alloying behaviour.

#### 2.1.2. Bulk concentration–concentration fluctuations in the long-wavelength limit, $S_{cc}^b(0)$

$S_{cc}^b(0)$  is an essential microscopic function which has been widely used to study the nature of atomic order in binary liquid alloys [24,25]. This function is related to  $\frac{G_M}{RT}$  and activity  $a_A$  via the following equation:

$$S_{cc}^b(0) = Nk_B T \left( \frac{\partial^2 G_M}{\partial c^2} \right)_{T,P,N}^{-1} = (1-c) a_A \left( \frac{\partial a_A}{\partial c} \right)_{T,P,N}^{-1} \quad (5)$$

The expression for bulk  $S_{cc}^b(0)$  in the framework of QCA model for regular solution is [7]:

$$S_{cc}^b(0) = \frac{c_A c_B}{[1 + (z/2\beta)(1 - \beta)]} \quad (6)$$

The ideal values of bulk concentration–concentration fluctuations,  $S_{cc}^b(0, id)$  corresponding to the values of concentration–concentration fluctuations when the ordering energy is zero is usually computed from:

$$S_{cc}^b(0, id) = c_A c_B \quad (7)$$

The deviation of  $S_{cc}^b(0)$  from  $S_{cc}^b(0, id)$  gives information on the behaviour of liquid binary alloys [26].

#### 2.1.3. Bulk Warren–Cowley short range order parameter, $\alpha_i$

The parameter often employed to quantify the degree of chemical order in the alloy melt is the bulk Warren–Cowley short range order parameter,  $\alpha_i^b$  [23]. This parameter gives insight into the local arrangement of the atoms in the molten alloy [23]. Although it is difficult to obtain the experimental values of  $\alpha_i^b$ , theoretical values of this parameter are easily obtain via conditional probability [A/B] which defines the probability of finding an A-atom as a nearest neighbour of a given B-atom.

The expression relating  $\alpha_i^b$  and the bulk  $S_{cc}(0)$  is given as [27,28]

$$\frac{S_{cc}^b(0)}{c_A c_B} = \frac{1 + \alpha_1^b}{1 - (Z-1)\alpha_1^b} \quad (8)$$

#### 2.1.4. Entropy of mixing, $\frac{S_M}{R}$ and enthalpy of mixing, $\frac{H_M}{RT}$

The calculations of enthalpy and entropy of mixing are of immense relevance since they will likely provide information on the temperature dependence of the ordering energy [25]. The expression for the entropy of mixing,  $\frac{S_M}{R}$  in the framework of QCA model for regular solution is given by

$$\frac{S_M}{R} = -(c_A \ln c_A + c_B \ln c_B + c_A \ln \gamma_A + c_B \ln \gamma_B) - \frac{8c_A^2 c_B^2 \eta^2}{\xi_1 \xi_2 \xi_3} \left[ \frac{1}{k_B} \frac{dW}{dT} - \frac{W}{k_B T} \right] \quad (9)$$

where in Eq. (9)  $\eta = \exp\left(\frac{W}{zk_B T}\right)$ ;  $\xi_1 = \beta - 1 + 2c_A$ ;  $\xi_2 = 1 + \beta$  and  $\xi_3 = \beta + 1 - 2c_A$

Also, the expression for enthalpy of mixing in the framework of QCA model for regular solution is given by

$$\frac{H_M}{RT} = -\frac{8c_A^2 c_B^2 \eta^2}{\xi_1 \xi_2 \xi_3} \left[ \frac{1}{k_B} \frac{dW}{dT} - \frac{W}{k_B T} \right] \quad (10)$$

It is obvious that if the ordering energy is independent of temperature (i.e.  $\frac{dW}{dT} = 0$ ), Eqs. (9) and (10) will respectively become

$$\frac{S_M}{R} = -(c_A \ln c_A + c_B \ln c_B + c_A \ln \gamma_A + c_B \ln \gamma_B) - \frac{8c_A^2 c_B^2 \eta^2}{\xi_1 \xi_2 \xi_3} \left[ -\frac{W}{k_B T} \right] \quad (11)$$

$$\frac{H_M}{RT} = -\frac{8c_A^2 c_B^2 \eta^2}{\xi_1 \xi_2 \xi_3} \left[ -\frac{W}{k_B T} \right] \quad (12)$$

## 2.2. Surface concentration and surface tension

It has been reported that surface segregation which is usually indicated by the preferential enrichment of the surface by the atoms of one of the two component elements in a binary alloy is influenced by the interaction among the atoms as well as the surface tension effects [29,31–35]. It has well been noted that a lot of properties such as mechanical behaviour, kinetics of phase transformation, catalytic activity and thin-film which are technologically relevant cannot be explained without an understanding of what is/are responsible for surface segregation and variation of surface tension [29].

Using the QCA model in conjunction with the expression for activity coefficients obtained via Fowler–Guggenheim method, the pair of equation relating the surface tension,  $\sigma$  and surface concentration,  $c^S$  for regular alloys is [36–39]:

$$\begin{aligned} \sigma &= \sigma_A + \frac{k_B T(2-gZ)}{2\alpha} \ln \frac{c_A^S}{c_A} + \frac{Zk_B T}{2\alpha} \left[ g \ln \frac{(\beta^S - 1 + 2c_A^S)(1 + \beta)}{(\beta - 1 + 2c_A)(1 + \beta^S)} - q \ln \frac{(\beta - 1 + 2c_A)}{(1 + \beta)c_A} \right] \\ &= \sigma_B + \frac{k_B T(2-gZ)}{2\alpha} \ln \frac{c_B^S}{c_B} + \frac{Zk_B T}{2\alpha} \left[ g \ln \frac{(\beta^S + 1 - 2c^S)(1 + \beta)}{(\beta + 1 - 2c_A)(1 + \beta^S)} - q \ln \frac{\beta + 1 - 2c_A}{(1 + \beta)c_B} \right] \end{aligned} \quad (13)$$

where in Eq. (13)  $T$  is the temperature of interest in Kelvin;  $g$  and  $q$  are the surface coordination fractions and they are defined such that:  $g + 2q = 1$  and for the usually assumed closed-packed structure,  $g = 0.5$  while  $q = 0.25$ ;  $\sigma_i$  ( $i = A$  or  $B$ ) are the surface tension of the pure components A and B [30,34,38,39,43];  $\alpha$  is the mean atomic surface area and is usually computed from the relation:  $\alpha = \sum_i c_i \alpha_i$  and  $\alpha_i = 1.102 \left( \frac{\Omega_i}{N_A} \right)^{2/3}$ ;  $N_A$

is the Avogadro's number and  $\Omega_i$  is the atomic volume of component  $i$ ;  $c_A$  and  $c_B$  are the bulk concentrations of A and B components;  $c_A^s$  and  $c_B^{sup}$  are the surface concentrations of A and B components;  $\beta$  is obtained from:  $\beta = [1 + 4c(1 - c)(\zeta^2 - 1)]^{1/2}$  with  $\zeta = \exp(\frac{W^s}{2k_bT})$  and  $W^s$  is the ordering energy at the surface (=  $W$ , the bulk ordering energy on the premise that ordering energy is an invariant property of a system [28,34,41]);  $\beta^s$  is the function obtained from  $\beta$  by substituting the bulk concentration,  $c$  and the coordination number,  $z$  by the surface concentration,  $c^s$  and surface coordination number,  $z^s$  (using the relation:  $z^s = z(g + q)$ ) respectively.

2.3. Surface concentration–concentration fluctuations and Warren–Cowley short range order parameter

In order to compare the behaviour of concentration–concentration fluctuations and Warren–Cowley short range order parameter in the bulk and at the interface of each of the two alloys of current interest, there is a need for the determination of concentration–concentration fluctuations and Warren–Cowley short range order parameter at the interface [28]. On the basis of the earlier works of Singh et al. in refs. [1,44] for the bulk phase, an expression for the concentration–concentration fluctuations at the surface obtained via solving the surface grand partition function is given by [28,34,42]

$$S_{cc}^s(0) = \frac{C_A^s C_B^s}{[1 + (Z^s/2\beta^s)(1 - \beta^s)]} \tag{14}$$

In the case of an ideal mixing (i.e.  $W = 0$ ), Eq. (14) becomes [28,34]

$$S_{cc}^s(0, ideal) = C_A^s C_B^s \tag{15}$$

The expression for surface Warren–Cowley short range order parameter,  $\alpha_1^s$  deduced from Eq. (8) is given by [28]

$$\frac{S_{cc}^s(0)}{C_A^s C_B^s} = \frac{1 + \alpha_1^s}{1 - (Z^s - 1)\alpha_1^s} \tag{16}$$

3. Results

The values of the respective  $W$  employed in this work for each of the two alloys we worked on are shown in Table 1. These were the values that reproduced to a reasonable extent the thermodynamic experimental data of  $\frac{G_M}{RT}$  (from ref. [45]) and the experimental data of  $S_{cc}^b(0)$  (the experimental values of  $S_{cc}^b(0)$  for Cd–Hg and Cd–Mg were respectively computed via experimental activity,  $a_A$  and experimental free energy of mixing,  $\frac{G_M}{RT}$  taken from ref. [45] using Eq. (5)).

Eqs. (1), (6) and (8) have been used to compute  $\frac{G_M}{RT}$ ,  $S_{cc}^b(0)$  and  $\alpha_1^b$  in that order. The  $S_{cc}^b(0, id)$  was computed from Eq. (7). Figs. 1 and 2 show the results of these computations. We observed that there are remarkable agreement between the computed  $\frac{G_M}{RT}$ ,  $S_{cc}^b(0)$  and their respective experimental data.

We computed  $\frac{S_M}{R}$  and  $\frac{H_M}{RT}$  for the two alloys as shown in Figs. 3 and 4 using Eqs. (9) and (10) on one hand, and using Eqs. (11) and (12) on the other hand. The values of the respective  $\frac{dW}{dT}$  employed in our computations (shown in Table 1) were obtained by fitting the computed values of  $\frac{S_M}{R}$  and  $\frac{H_M}{RT}$  with the available experimental data taken from ref [45]. We observed that in the two alloys, while the plots resulting

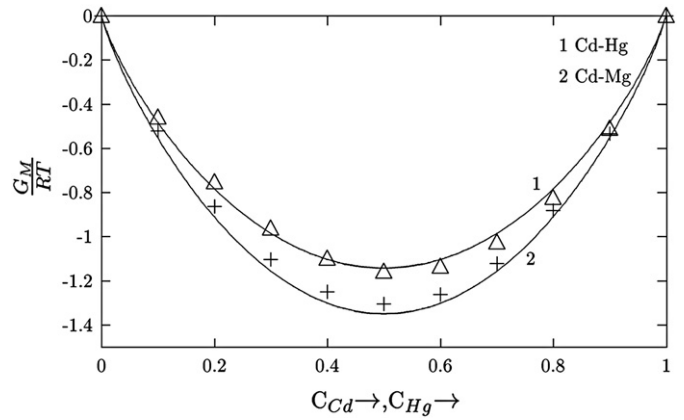


Fig. 1. Concentration dependence of free energy of mixing,  $\frac{G_M}{RT}$  for Cd–Hg (curve 1) and Cd–Mg (curve 2) liquid alloys at 600 K and 923 K respectively, computed from Eq. (1). The bulk concentration of Cd in Cd–Mg is represented by  $C_{Cd}$  while  $C_{Hg}$  is the bulk concentration of Hg in Cd–Hg. The triangles are the experimental  $\frac{G_M}{RT}$  for Cd–Hg while the crosses are the experimental  $\frac{G_M}{RT}$  for Cd–Mg.

from Eqs. (11) and (12) are in very poor agreement with the experimental data, the plots resulting from Eqs. (9) and (10) show remarkable agreement between the experimental data and the computed values.

The concentration–concentration fluctuations and the Warren–Cowley short range order parameter at the surface for the two alloys have been computed via Eqs. (14) and (16). The ideal concentration–concentration fluctuations at the surface were computed using Eq. (15). The results of these are shown in Figs. 5 and 6. These plots show a contrast in the pair of  $S_{cc}^b(0)$  and  $S_{cc}^s(0)$  and in the pair of  $\alpha_1^b$  and  $\alpha_1^s$  for the two alloys.

Eq. (13) has been solved numerically to compute the concentration dependence of surface tension,  $\sigma$  and the surface composition,  $C_i^s$  as a function of bulk composition for Cd–Mg and Cd–Hg at 923 K and 600 K respectively. The results obtained when the parameters in Tables 1 and 2 were used are shown in Figs. 7 and 8. The isothermal plots (presented for the purpose of additional comparative perusal), of the two systems in Fig. 8 show that the surface tension of both Cd–Hg and Cd–Mg liquid alloys decreases with the addition of Cd and Hg respectively and remains lower than the ideal values at all bulk concentrations.

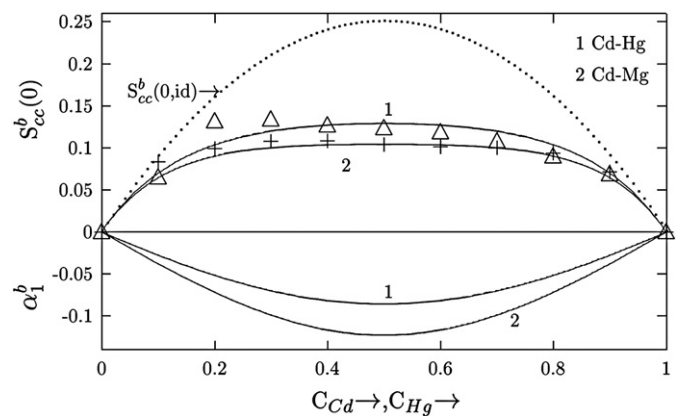


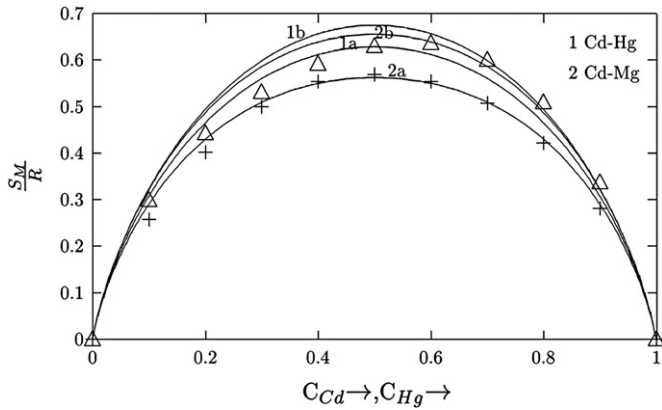
Fig. 2. Concentration dependence of the bulk concentration–concentration fluctuations,  $S_{cc}^b(0)$  and bulk Warren–Cowley short range order parameter,  $\alpha_1^b$  for Cd–Hg (curve 1) and Cd–Mg (curve 2) liquid alloys at 600 K and 923 K respectively. These two curves were computed respectively using Eqs. (6) and (8). The dots, computed from Eq. (7), represent the ideal values of the bulk concentration–concentration fluctuations,  $S_{cc}^b(0, id)$ .  $C_{Cd}$  is the bulk concentration of Cd in Cd–Mg while  $C_{Hg}$  is the bulk concentration of Hg in Cd–Hg. The triangles are the experimental  $S_{cc}^b(0)$  for Cd–Hg while the crosses are the experimental  $S_{cc}^b(0)$  for Cd–Mg.

Table 1

Basic parameters obtained from the bulk property calculations for Cd–Hg and Cd–Mg at temperatures of 600 K and 923 K respectively<sup>a</sup>.

System	$W/k_bT$	$dW/dT$
Cd–Hg	– 1.7200	0.1710
Cd–Mg	– 2.4700	0.3320

<sup>a</sup> The values of these parameters are obtained by thermodynamic fitting.



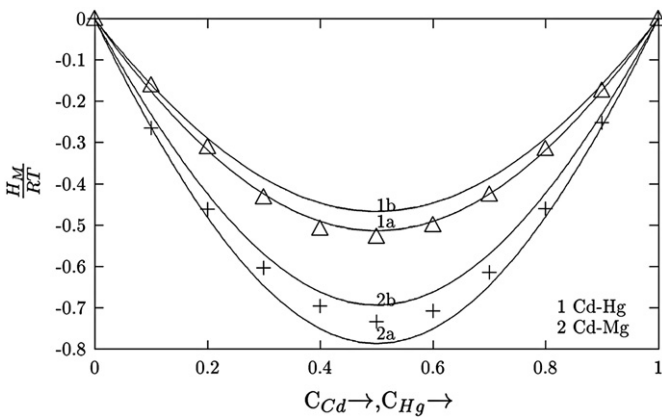
**Fig. 3.** Concentration dependence of entropy of mixing,  $\frac{S_M}{R}$  for Cd-Hg and Cd-Mg liquid alloys at 600 K and 923 K respectively, using Eqs. (9) and (11). Curves 1a and 2a are the respective  $\frac{S_M}{R}$  for Cd-Hg and Cd-Mg liquid alloys, using Eq. (9) while curves 1b and 2b are the respective  $\frac{S_M}{R}$  for Cd-Hg and Cd-Mg liquid alloys, using Eq. (11).  $C_{Cd}$  is the bulk concentration of Cd in Cd-Mg while  $C_{Hg}$  is the bulk concentration of Hg in Cd-Hg. The triangles are the experimental  $\frac{S_M}{R}$  for Cd-Hg while the crosses are the experimental  $\frac{S_M}{R}$  for Cd-Mg.

**4. Discussion**

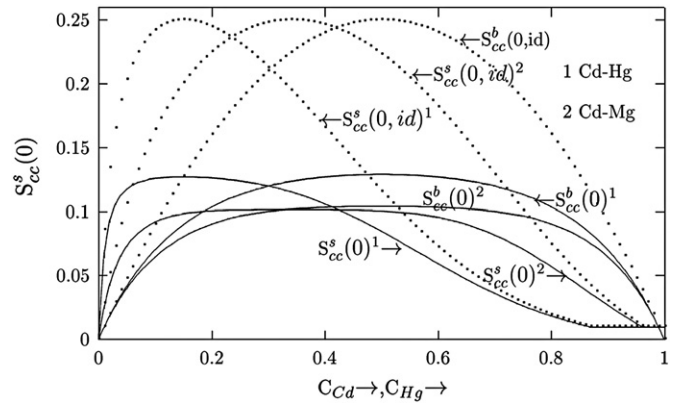
The implication of the W in Table 1 being negative for the two alloys is that they are both chemically ordered. However, the degree of chemical order in Cd-Mg (with  $\frac{W}{k_B T} = -2.4700$ ) is about 30% more than that in Cd-Hg (with  $\frac{W}{k_B T} = -1.7200$ ).

The remarkable agreement between the computed  $\frac{G_M}{RT}$ ,  $S_{cc}^b(0)$  and their respective experimental data (as in Figs. 1 and 2) confirms that the choice of  $\omega$  for the two alloys is quite reasonable. In addition, in view of the following observations, these two figures also show that although the two alloys are both chemically ordered, their chemical order is weak and Cd-Mg is more heterocoordinated than Cd-Hg:

1. In Fig. 1 the minimum of  $\frac{G_M}{RT}$  for Cd-Mg is about  $-1.3$  while that of Cd-Hg is about  $-1.1$ . This is an indication that Cd-Mg is more heterocoordinated than Cd-Hg since in an extremely or strongly interacting binary alloy,  $\frac{G_M}{RT} \leq -3.0$  [3,46].
2. In Fig. 2 the deviation  $[S_{cc}^b(0, id) - S_{cc}^b(0)]$  is greater in Cd-Mg than in Cd-Hg. This implies that the former is more chemically ordered than the later since it has been established that when  $S_{cc}^b(0, id)$  is greater than  $S_{cc}^b(0)$  in a binary alloy it is a signature of heterocoordination.



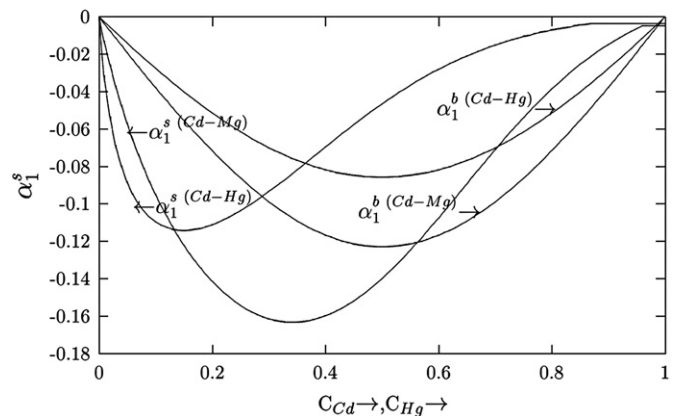
**Fig. 4.** Concentration dependence of enthalpy of mixing,  $\frac{H_M}{R}$  for Cd-Hg and Cd-Mg liquid alloys at 600 K and 923 K respectively, using Eqs. (10) and (12). Curves 1a and 2a are the respective  $\frac{H_M}{R}$  for Cd-Hg and Cd-Mg liquid alloys, using Eq. (10) while curves 1b and 2b are the respective  $\frac{H_M}{R}$  for Cd-Hg and Cd-Mg liquid alloys, using Eq. (12).  $C_{Cd}$  is the bulk concentration of Cd in Cd-Mg while  $C_{Hg}$  is the bulk concentration of Hg in Cd-Hg. The triangles are the experimental  $\frac{H_M}{R}$  for Cd-Hg while the crosses are the experimental  $\frac{H_M}{R}$  for Cd-Mg.



**Fig. 5.** Computed values of the bulk concentration-concentration fluctuations,  $S_{cc}^b(0)$  and concentration-concentration fluctuations at the surface,  $S_{cc}^s(0)$  for Cd-Hg and Cd-Mg liquid alloys at 600 K and 923 K respectively. The dots labelled  $S_{cc}^b(0, id)$  represent the ideal values of the bulk concentration-concentration fluctuations computed from Eq. (7). The curve labelled  $S_{cc}^b(0)^1$  represents the computed values of the bulk concentration-concentration fluctuations for Cd-Hg obtained from Eq. (6). The curve labelled  $S_{cc}^b(0)^2$  represents the computed values of the bulk concentration-concentration fluctuations for Cd-Mg obtained from Eq. (6). The dots labelled  $S_{cc}^s(0, id)^1$  represent the ideal values of the concentration-concentration fluctuations at the surface for Cd-Hg computed from Eq. (15). The dots labelled  $S_{cc}^s(0, id)^2$  represent the ideal values of the concentration-concentration fluctuations at the surface for Cd-Mg computed from Eq. (15). The curve labelled  $S_{cc}^s(0)^1$  represents the computed values of the concentration-concentration fluctuations at the surface for Cd-Hg obtained from Eq. (14). The curve labelled  $S_{cc}^s(0)^2$  represents the computed values of the concentration-concentration fluctuations at the surface for Cd-Mg obtained from Eq. (14).  $C_{Cd}$  is the bulk concentration of Cd in Cd-Mg while  $C_{Hg}$  is the bulk concentration of Hg in Cd-Hg.

3. A perusal of Fig. 2 shows that the minimum of  $\alpha_1^b$  for Cd-Mg is about  $-0.12$  (i.e. 12% chemical order) while that of Cd-Hg is about  $-0.08$  (i.e. 8% chemical order). This reveals that Cd-Mg is about 33% more heterocoordinated than Cd-Hg since in Section 2.1.3, we mentioned that a complete ordering is indicated when  $\alpha_1^b = -1$ .

The implication of Eqs. (11) and (12) employed in the computation of  $\frac{S_M}{R}$  and  $\frac{H_M}{RT}$  is that these two quantities can be evaluated merely from the knowledge of the ordering energy. However, the very poor agreement between the computed values obtained from these equations and the experimental data (shown in Figs. 3 and 4) for the two alloys suggests the importance of the ordering energy dependence on temperature for the two alloys. A look at the plots (i.e. plots 1a and 2a in Figs. 3 and 4) resulting from Eqs. (9) and (10) which incorporated temperature dependence of ordering energy (i.e.  $\frac{dW}{dT}$ ) shows a remarkable



**Fig. 6.** Concentration dependence of the bulk Warren-Cowley short range order parameter,  $\alpha_1^b$  (computed from Eq. (8)) and surface Warren-Cowley short range order parameter,  $\alpha_1^s$  (computed from Eq. (16)) for Cd-Hg and Cd-Mg liquid alloys at 600 K and 923 K respectively.  $C_{Cd}$  is the bulk concentration of Cd in Cd-Mg while  $C_{Hg}$  is the bulk concentration of Hg in Cd-Hg.

**Table 2**  
Essential parameters for the surface property calculation in the statistical mechanics model for Cd–Hg and Cd–Mg at temperatures of 600 K and 923 K respectively<sup>a</sup>.

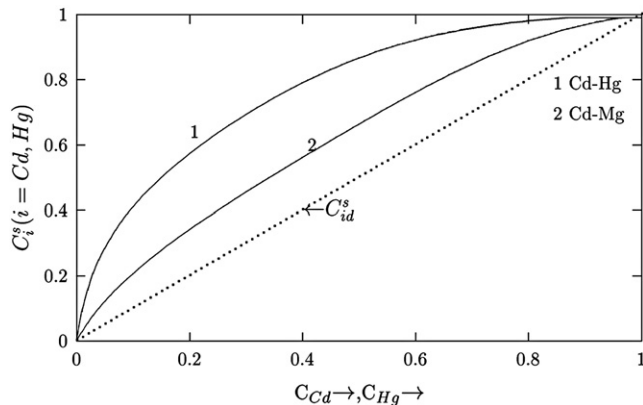
Atom	$\sigma(N/m)$	$d\sigma \times 10^{-3}(N/m/K)$
Cd at 600 K	0.5685	−0.2600
Hg at 600 K	0.4249	−0.2000
Cd at 923 K	0.4845	−0.2600
Mg at 923 K	0.5591	−0.3500

<sup>a</sup> The values of these parameters are obtained from [40].

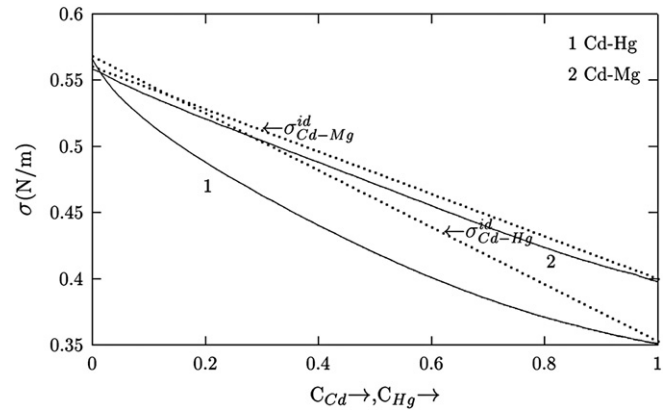
agreement between the experimental data and the computed values which confirms the temperature dependence of the ordering energy of the two alloys.

The contrast in the pair of  $S_{cc}^b(0)$  and  $S_{cc}^s(0)$  and the pair of  $\alpha_i^b$  and  $\alpha_i^s$  for the two alloys (as seen in Figs. 5 and 6) is not surprising due to the difference between the bulk and the surface compositions, as evident in Fig. 7 [28,34]. Also, Fig. 5 shows that just as  $S_{cc}^b(0) < S_{cc}^s(0, id)$ , so also is  $S_{cc}^s(0) < S_{cc}^s(0, id)$  throughout the entire composition of Cd in Cd–Mg and throughout the entire composition of Hg in Cd–Hg which indicate the presence of chemical order both in the bulk and on the surfaces of the two alloys. Fig. 5 further shows that the difference between  $S_{cc}^s(0)$  and  $S_{cc}^s(0, id)$  in Cd–Mg is more than that of Cd–Hg and this confirms the earlier observation that Cd–Mg is more heterocoordinated than Cd–Hg. In Fig. 6, both  $\alpha_i^b$  and  $\alpha_i^s$  are negatives for the two alloys which means that there is chemical order both in the bulk and on the surfaces of the two alloys. In addition, the minimum of  $\alpha_i^s$  of Cd–Mg (about −0.16 which implies 16% order) which is about 25% more than the minimum of  $\alpha_i^s$  of Cd–Hg (about −0.12 which implies 12% order) is another evidence that the former is more heterocoordinated than the latter.

The study of surface concentration as shown in Fig. 7 shows the usual pattern of surface concentration increasing with increasing bulk compositions. This indicates that Cd-atoms (having lower value of surface tension relative to Mg-atoms in Cd–Mg) and Hg-atoms (having lower value of surface tension relative to Cd-atoms in Cd–Hg) segregate respectively at the surfaces of Cd–Mg and Cd–Hg liquid alloys throughout the entire bulk compositions. The high degree of segregations of Cd-atoms and Hg-atoms on the respective surfaces of Cd–Mg and Cd–Hg systems (as signalled by the large deviations between their computed surface concentration plots and the ideal solution plot) is a confirmation of the presence of chemical short range order at the surfaces of the two systems and that the contribution of chemical short range order to the segregation of Cd-atoms and Hg-atoms on the respective surfaces of Cd–Mg and Cd–Hg is quite



**Fig. 7.** Computed values of the surface concentration,  $C_{Hg}^s$  for Cd–Hg (curve 1) liquid alloy at 600 K and surface concentration,  $C_{Cd}^s$  for Cd–Mg (curve 2) liquid alloy at 923 K. These two curves were computed from Eq. (13). The dots represent the ideal values of the surface concentration,  $C_{id}^s$  computed from:  $C_{id}^s = C^b$ . The bulk concentration of Cd in Cd–Mg is represented by  $C_{Cd}$  while  $C_{Hg}$  is the bulk concentration of Hg in Cd–Hg.



**Fig. 8.** Computed values of the surface tension,  $\sigma$  for Cd–Hg (curve 1) and Cd–Mg (curve 2) liquid alloys at 600 K and 923 K respectively, obtained from Eq. (13). The dots labelled  $\sigma_{Cd-Mg}^{id}$  and  $\sigma_{Cd-Hg}^{id}$  represent the ideal values of the surface tension of the Cd–Mg and Cd–Hg respectively, obtained from the relation:  $\sigma_i^{id} = \sigma_A C_A + \sigma_B C_B$  and  $\sigma_i$  ( $i = A$  or  $B$ ) is as defined in Eq. (13).  $C_{Cd}$  is the bulk concentration of Cd in Cd–Mg while  $C_{Hg}$  is the bulk concentration of Hg in Cd–Hg.

significant. Also, although the deviation of the computed surface concentration from the ideal solution at the upper part of the higher bulk compositions of the two systems is about the same, we observed that outside these compositions, the degree of segregation of Hg-atoms on the surface of Cd–Hg liquid alloy is more than that of the Cd–Mg system. This is possibly a corroborating evidence that Cd–Mg is more heterocoordinated than Cd–Hg.

Although, due to lack of surface tension experimental data we could not compare our computed surface tension in Fig. 8 with the experimental data, nonetheless, we observed that the isothermal plots of surface tension of the two systems exhibit negative deviations from the ideal values (i.e. the proportional mathematical addition of the pure components' surface tension) as it is the case with most binary liquid mixtures [40]. This suggests that Cd-atoms segregate on the surface of Cd–Mg while Hg-atoms segregate on the surface of Cd–Hg. Also, from the figure we observed that while there is not much deviation from the ideal values of the surface tension and the calculated surface tension of Cd–Mg, there is a significant deviation between the ideal values of the surface tension and the calculated values of the surface tension of Cd–Hg. This implies that the rate of decrease of  $\sigma$  in Cd–Mg system is comparatively smaller than that of  $\sigma$  in Cd–Hg and might be due to the presence of more chemical short range order at the surface of Cd–Mg than at the surface of Cd–Hg, as observed earlier in Fig. 6. The absence of irregularities in the form of minimum, maximum or inflection point in the isothermal plots of surface tension of the two alloys is a signature of the absence of stoichiometric intermetallic compound formation in the two systems. However, going by the phase diagram of Cd–Hg as in ref. [45], intermetallic compound  $Cd_2Hg$  or  $CdHg_2$  exists in the solid phase of Cd–Hg which suggests the possibility of a shoulder in the surface tension isothermal of Cd–Hg at about 30%Hg or 60%Hg compositions. This apparent disparity is either attributable to the fact that Cd–Hg liquid alloy is a weakly interacting system (as the case with Al–Cu [9]) or is a reminiscent of the fact that the question of whether the surface tension of a liquid phase will reflect the ordering phenomenon manifested by corresponding ordered solid phase or not is still a controversial issue [9].

### 5. Conclusions

Our theoretical study of the energetics and alloying behaviour of Cd–Hg and Cd–Mg liquid alloys at 600 K and 923 K respectively reveals that they are both heterocoordinated in the bulk and surface throughout the entire composition of Hg in Cd–Hg and Cd in Cd–Mg. Also, although the chemical order in the two alloys is weak (both in the bulk and on the

surface), the chemical order in Cd–Mg is between 25% and 33% more than that in Cd–Hg. This study has also confirmed the temperature dependence of the ordering energy,  $\omega$ .

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### References

- [1] R.N. Singh, I.K. Mishra, V.N. Singh, J. Phys. Condens. Matter 2 (1990) 8457.
- [2] L.C. Prasad, R.N. Singh, Phys. Chem. Liq. 22 (1990) 1–9.
- [3] R.N. Singh, Can. J. Phys. 65 (1987) 309.
- [4] R. Novakovic, E. Ricci, F. Gnecco, D. Giuranno, G. Borzone, Surf. Sci. 599 (2005) 230.
- [5] L.C. Prasad, A. Mikula, Physica B373 (2006) 64.
- [6] O.E. Awe, Y.A. Odusote, L.A. Hussain, O. Akinlade, J. Thermochim. Acta 519 (2011) 1.
- [7] R.N. Singh, D.K. Pandey, S. Sinha, N.R. Mitra, P.L. Srivastava, Physica B145 (1987) 358.
- [8] A.B. Bhatia, R.N. Singh, Phys. Chem. Liq. 11 (1982) 285.
- [9] I. Egry, E. Ricci, R. Novakovic, S. Ozawa, Adv. Colloid Interface Sci. 159 (2010) 198.
- [10] WebElements: the periodic table on the web. Retrieved on January 6, 2012 from [www.webelements.com/cadmium/crystal-structure.html](http://www.webelements.com/cadmium/crystal-structure.html).
- [11] WebElements: the periodic table on the web. Retrieved on January 6, 2012 from [www.webelements.com/magnesium/crystal-structure.html](http://www.webelements.com/magnesium/crystal-structure.html).
- [12] WebElements: the periodic table on the web. Retrieved on January 6, 2012 from [www.webelements.com/mercury/crystal-structure.html](http://www.webelements.com/mercury/crystal-structure.html).
- [13] P.P. Singh, Phys. Rev. Lett. 72 (15) (1994) 2446.
- [14] S.C. Hansen, Calphad 22 (3) (1998) 359.
- [15] Health, safety executive, Cadmium and you—working with cadmium—are you at risk? Retrieved on December 7, 2011 from [www.hse.gov.uk/pubns/indg391.pdf](http://www.hse.gov.uk/pubns/indg391.pdf). Sept. 20, 2011.
- [16] 8th International cadmium conference (Nov. 10–13, 2011, Kunming, China), Working towards a sustainable future, 2011, Retrieved on December 7, 2011 from [www.cadmium.org/pg-n.php?id-menu=15](http://www.cadmium.org/pg-n.php?id-menu=15).
- [17] A.K. Mishra, M. Milanarun, High Temp. Mater. Processes 24 (1) (2005) 47.
- [18] M. Asta, R. McCormack, D. de Fontaine, Phys. Rev. B48 (1993) 748.
- [19] T. Tanaka, N.A. Gokcen, Z. Morita, Z. Metallkd. 81 (1) (1990) 49.
- [20] A. Marbeuf, R. Druilhe, R. Triboulet, G. Patriarche, J. Cryst. Growth 117 (1–4) (1992) 10.
- [21] J. Yang, N.J. Silk, A. Watson, A.W. Bryant, T.G. Chart, B.B. Argent, Calphad 19 (3) (1995) 415.
- [22] J.W. McClure, J. Martyniuk, Phys. Rev. Lett. 29 (1972) 1095.
- [23] L.C. Prasad, R.N. Singh, V.N. Singh, S.K. Chatterjee, Physica B215 (1995) 225.
- [24] O.E. Awe, O. Akinlade, L.A. Hussain, Surf. Sci. 600 (2006) 2122.
- [25] R.N. Singh, I.S. Jha, D.K. Pandey, J. Phys. Condens. Matter 5 (1993) 2469.
- [26] R. Novakovic, E. Ricci, J. Alloys Compd. 452 (2008) 167.
- [27] R. Novakovic, D. Giuranno, E. Ricci, T. Lanata, Surf. Sci. 602 (2008) 1957.
- [28] R. Novakovic, E. Ricci, D. Giuranno, F. Gnecco, Surf. Sci. 515 (2002) 377.
- [29] L.C. Prasad, A. Mikula, Physica B373 (2006) 142.
- [30] R. Novakovic, T. Tanaka, M.L. Muolo, J. Lee, A. Passerone, Surf. Sci. 591 (2005) 56.
- [31] K.S. Yeum, R. Speiser, D. Poirier, Metall. Trans. 208 (1989) 693.
- [32] K. Okajima, H. Sakao, Trans. Jpn. Inst. Met. 23 (3) (1982) 111.
- [33] Z. Moser, M. Kucharski, J. Non-Cryst. Solids 156–158 (1993) 369.
- [34] L.C. Prasad, R.N. Singh, Phys. Rev. B44 (1991) 13768.
- [35] L.C. Prasad, R.N. Singh, V.N. Singh, G.P. Singh, J. Phys. Chem. B102 (1998) 921.
- [36] R.H. Fowler, E.A. Guggenheim, Statistical Thermodynamics, University Press, Cambridge, 1990.
- [37] R. Novakovic, T. Tanaka, Physica B371 (2006) 223.
- [38] L.C. Prasad, R.N. Singh, G.P. Singh, Phys. Chem. Liq. 27 (1994) 179.
- [39] O.E. Awe, Int. J. Mater. Res. (formerly Z. Metallkd.) 100 (2009) 11.
- [40] T. Iida, R.L.L. Guthrie, The Physical Properties of Liquid Metals, Clarendon Press, Oxford, 1988.
- [41] R. Novakovic, E. Ricci, D. Giuranno, A. Passerone, Surf. Sci. 576 (2005) 175.
- [42] B.C. Anusionwu, O. Akinlade, L.A. Hussain, J. Alloys Compd. 278 (1998) 175.
- [43] R. Novakovic, D. Giuranno, E. Ricci, S. Delsante, D. Li, G. Borzone, Surf. Sci. 605 (2011) 248.
- [44] R.N. Singh, I.K. Mishra, Phys. Chem. Liq. 18 (1988) 303.
- [45] R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Kelley, Selected Values of the Thermodynamic Properties of the Binary Alloys, American Society for Metals, Metal Park, OH, 1973.
- [46] R.N. Singh, N.H. March, in: J.H. Westbrook, R.L. Fleischer (Eds.), Intermetallic Compounds, Principles and Practice, vol. 1, John Wiley and Sons, New York, 1995, p. 661.