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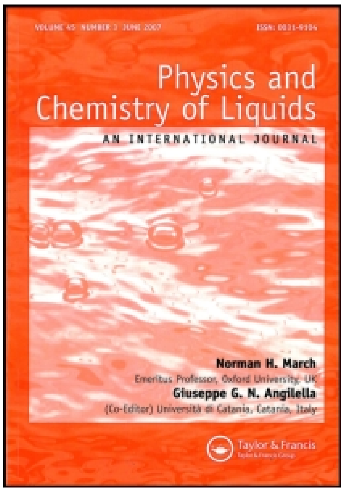

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Segregation and surface properties of In–Zn liquid alloys

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The segregation tendencies of In–Zn liquid alloys in the bulk and at the surface has been studied at temperatures of 692, 850 and 1000 K, using a statistical model based on an association of like-species. The strength of segregation in the bulk of this alloy appear to reduce exponentially with an increase in temperature. The surface tension values between 0.55 and 0.9 bulk atomic fraction of Zn showed an increase with the rise in temperature.

Keywords: Liquid alloys; Surface and interfaces

1. Introduction

In general, liquid binary alloys can be classified as compound-forming or phase-segregating. A very useful criterion for making this classification is the departure of the concentration dependence of the concentration–concentration fluctuation at the long wavelength limit $S_{cc}(0)$ from its ideal values. The ideal values of $S_{cc}(0)$ is obtained by $c(1-c)$. Here, c is the concentration of A atoms in an $A-B$ liquid alloy. A liquid binary alloy is considered to be phase-segregating or has a preference for a like-atom cluster in a concentration range where its $S_{cc}(0) > c(1-c)$. In the concentration range where $S_{cc}(0) < c(1-c)$, the liquid alloy is said to be compound-forming or has a preference for an unlike atom cluster, while, if $S_{cc}(0) = c(1-c)$, the alloy is regular with an ideal mixture of alloy components.

Studies have shown that compound-formation and phase-segregation in the bulk of a liquid binary alloy have some influence on their surface properties [1,2]. Such observations have motivated researchers to intensively investigate the chemical compositions in the neighbourhood of alloy surfaces [1,3]. These studies are essential from the point of view of understanding in a fundamental way, surface-related phenomena,

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such as heterogeneous catalysis, wettability at solder joints, epitaxial growth and corrosion, as well as the mechanical behaviour and kinetics of phase transformation.

Binary liquid alloys that exhibit compound-forming characteristics or chemical short-range order (CSRO) have been intensively studied [4–6], while those classes of liquid alloys that have phase-segregating characteristics, showing endothermic reactions and exhibiting large positive enthalpy of mixing have been investigated, albeit with a lesser degree of interest both from the experimental and theoretical perspectives [7]. In–Zn liquid alloys belong to this class of phase-segregating liquid alloys. In recent times, the surface properties of In–Zn alloys have become a subject of scientific interest because liquid In–Zn alloy is being considered as a candidate component in a lead free fluxless solder alternative, when liquid In–Zn alloy is alloyed with Sn [8–10]. To develop such a fluxless solder technology, a good knowledge of surface properties, especially the surface tension of the candidate alloy is necessary [8].

In this work therefore, the bulk thermodynamic properties of In–Zn liquid alloy is investigated with a view to observe the response of its segregating characteristics with an increase in temperature from near-melting point. In addition, the change in the surface properties of this alloy with temperature will be determined based on parameters obtained from bulk thermodynamic investigation of the liquid alloy. The bulk thermodynamic properties of this alloy is investigated using the statistical model of Singh and Sommer [11], which derives from the concept of association of like atom species. The formulations of Prasad *et al.* [12] which relates surface properties to bulk activity coefficients will be used to determine the surface properties of the liquid alloy at the temperatures of investigation. One of the advantages of this formulation is that it will help to bring out the influence of bulk interaction on the surface properties, at the desired temperatures.

In the next section, the essential expression for the theoretical models will be outlined. The results and discussions are presented in section 3, while conclusions will be given in section 4.

2. Theoretical outlines

A simple statistical model proposed by Singh and Sommer [11] for studying phase-separating liquid binary alloys assumes that a liquid binary A–B alloy consisting of N_A atoms of element A and N_B atoms of element B situated at equivalent sites, having short-ranged interaction effective only between the nearest neighbours forms a polyatomic matrix leading to the formation of like-atom clusters or self-associates of type μA and νB, where μ and ν are the number of atoms in the clusters of types A and B matrices, respectively.

The thermodynamic properties of this category of liquid alloys depends on the number of self-associates, $n = \mu/\nu$, $\mu > \nu$. Using the quasi chemical approximation, an expression for the Gibbs free energy is obtained as,

$$G_m = RT\,[c\ln c + (1-c)\ln(1-c) + c\ln(1-\xi) + \ln\Gamma] + c(1-c)\Gamma W \qquad (1)$$

where c is the concentration of atom A, $W = \mu w$, $\xi = 1 - 1/n$ and $\Gamma = 1/(1 - c\xi)$. w is the interchange energy. The activities of the alloy components can be determined from the general expression

$$RT\ln a_i = \left(\frac{\partial G_\mathrm{m}}{\partial N_i}\right)_{T,P,N} \tag{2}$$

Using equation (1) in (2), expressions for activity (a_i) of the alloy components are obtained as

$$\ln a_\mathrm{A} = \ln(c\Gamma(1-\xi)) + (1-c)\Gamma\xi + (1-c)^2\Gamma^2\frac{W}{RT} \tag{3}$$

$$\ln a_\mathrm{B} = \ln(c\Gamma) + c(1-\xi)\Gamma(1-n) + nc^2(1-\xi)\Gamma^2\frac{W}{RT} \tag{4}$$

where R is the molar gas constant and the activity coefficients (γ_i) can be obtained from the relation $\gamma_i = a_i/c_i$.

The expression for the bulk concentration–concentration fluctuations at the long wavelength limit ($S_\mathrm{cc}(0)$) is, in general, given as

$$S_\mathrm{cc}(0) = RT\left(\frac{\partial^2 G_\mathrm{m}}{\partial c^2}\right)^{-1}_{T,P,N} \tag{5}$$

Under the present formulation, the $S_\mathrm{cc}(0)$ is given by the expression

$$S_\mathrm{cc}(0) = \frac{c(1-c)}{1-c(1-c)g(n,W)} \tag{6}$$

where

$$g(n,W) = \frac{2n^2(W/RT) - (n-1)^2[c+n(1-c)]}{[c+n(1-c)]^3} \tag{7}$$

In the model for studying surface properties, a statistical–mechanical approach which derives from the concept of a layered structure near the interface was used by Prasad *et al.* [12] to obtain expressions for surface properties. The surface grand partition function Ξ^s is related to the surface tension σ by the expression

$$\Xi^\mathrm{s} = \exp\left(\frac{-A\sigma}{kT}\right) = \exp\left(\frac{-N^\mathrm{s}\sigma\alpha}{kT}\right) \tag{8}$$

where A is the surface area and α is the mean area of the surface per atom and is defined as $\alpha = A/N^\mathrm{s}$, and N^s is the total number of atoms at the surface. k is the Boltzmann constant.

Prasad *et al.* [12] gave the expression for surface tension of the binary alloys in terms of activity coefficient of the alloy components as

$$\sigma = \sigma_{\mathrm{A}} + \frac{kT}{\alpha}\ln\frac{c_{\mathrm{A}}^{\mathrm{s}}}{c_{\mathrm{A}}} - \frac{kT}{\alpha}\ln\gamma_{\mathrm{A}} + \left[p(c_{\mathrm{B}}^{\mathrm{s}})^2 + q(c_{\mathrm{B}})^2\right]\frac{w}{\alpha} \tag{9}$$

$$\sigma = \sigma_{\mathrm{B}} + \frac{kT}{\alpha}\ln\frac{c_{\mathrm{B}}^{\mathrm{s}}}{c_{\mathrm{B}}} - \frac{kT}{\alpha}\ln\gamma_{\mathrm{B}} + \left[p(c_{\mathrm{A}}^{\mathrm{s}})^2 + q(c_{\mathrm{A}})^2\right]\frac{w}{\alpha} \tag{10}$$

where, σ_{A} and σ_{B} are the surface tension values for the pure components A and B, respectively; c_i and c_i^{s} are the bulk and surface concentrations of the alloy components, respectively; γ_{A} and γ_{B} are the bulk activity coefficients of the alloy components and w is the interchange energy.

The surface $S_{\mathrm{cc}}(0)$ can be written as [13]

$$S_{\mathrm{cc}}^{\mathrm{s}}(0) = c_{\mathrm{A}}^{\mathrm{s}}c_{\mathrm{B}}^{\mathrm{s}}\left[1 + \left(\frac{z^{\mathrm{s}}}{2\beta^{\mathrm{s}}}\right)(1-\beta^{\mathrm{s}})\right]^{-1} \tag{11}$$

where

$$\beta^{\mathrm{s}} = \left\{1 + 4c_{\mathrm{A}}^{\mathrm{s}}c_{\mathrm{B}}^{\mathrm{s}}\left[\exp\left(\frac{2w}{z^{\mathrm{s}}kT}\right) - 1\right]\right\}^{1/2} \tag{12}$$

Here, z^{s} is the coordination number of the surface atoms which is obtained from $z^{\mathrm{s}} = (p+q)z$ and z is the coordination number in the bulk.

3. Results and discussion

The model proposed by Singh and Sommer [11] was first used to investigate the concentration dependence of some thermodynamic quantities of the In–Zn alloys at different temperatures. Firstly, the values of n and W/RT were determined by obtaining a simultaneous overall fit of the experimental activity and Gibb's free energy of mixing (G_{m}) at the different temperatures of investigation. The values of n and W/RT, obtained at the different temperatures are given in table 1. These values are now used to determine the concentration fluctuation at the long wavelength limit $S_{\mathrm{cc}}(0)$. These calculated $S_{\mathrm{cc}}(0)$ will be used to assess how segregation in this alloy changes with temperature (figures 1 and 2).

Table 1. Model parameters for In–Zn liquid alloy.

T (K)	N	$W/(RT)$
692	1.27	1.58
850	1.27	1.21
1000	1.27	0.93

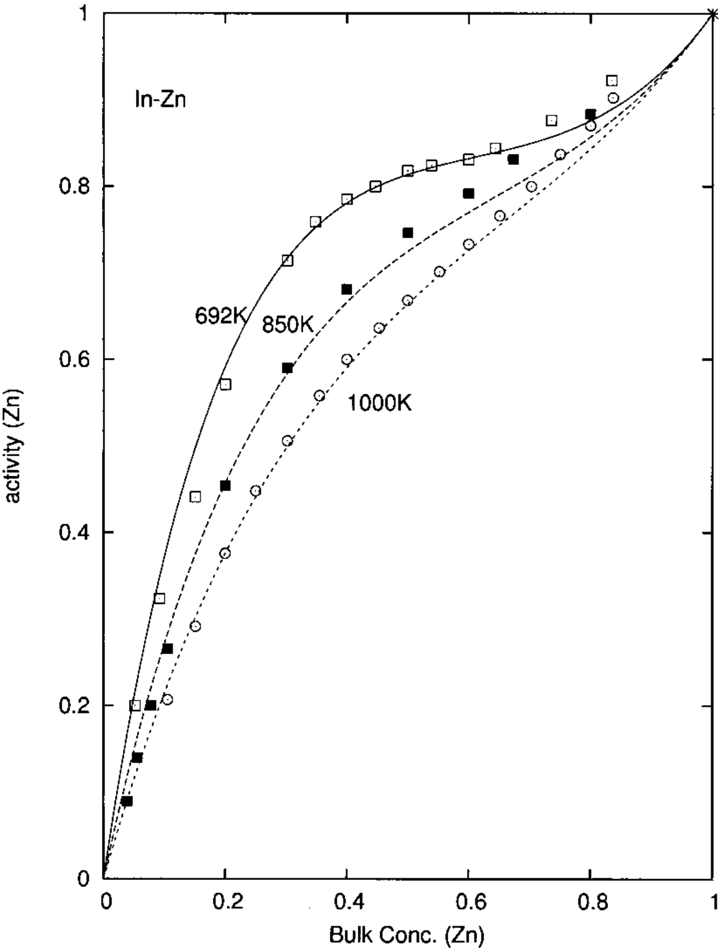

Figure 1. Activity (Zn) *vs.* atomic fraction of Zn for In–Zn liquid alloy. Points represent experimental values at the indicated temperatures. Lines are the corresponding calculated values at the indicated temperatures respectively.

The experimental data used in the calculation of the thermodynamic properties of In–Zn liquid alloy were from the work of Oelsen and Zuhlke [14] for 692 K, Moser [15] for 850 K and Hagiwara *et al.* [16] for 1000 K and were all reported and used by Lee [17]. It can be observed that the parameters reproduced fairly well the experimental values of activity and free energy of mixing at the indicated temperatures. The positive departure from ideality of the activity values is seen to decrease with increasing temperature, while the observed asymmetry in the free energy of mixing at 692 K was persistent and can still be slightly observed at the temperature of 1000 K. The trend of these changes suggests that though the local order in the In–Zn alloy appear to be reducing in strength, it persists even at a temperature of 1000 K.

To determine the strengths of segregation in the In–Zn alloy at different temperatures, the concentration fluctuation at the long wavelength limit $S_{cc}(0)$ calculated from equation (6) is used. The experimental $S_{cc}(0)$ was also determined and used

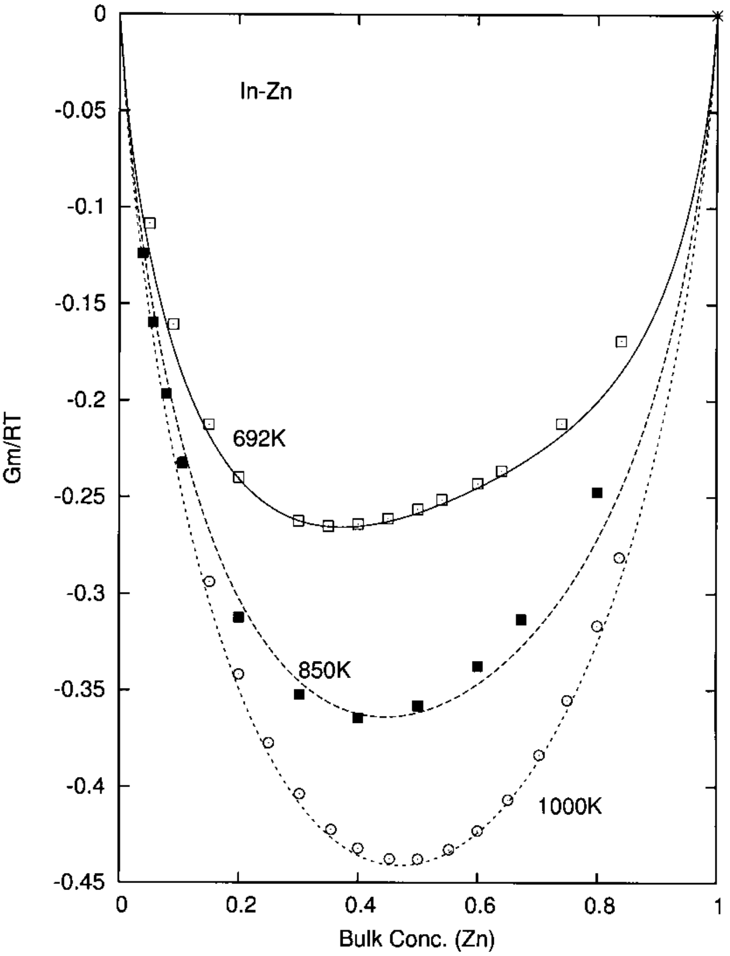

Figure 2. G/RT *vs.* atomic fraction of Zn for In–Zn liquid alloy. Points represent experimental values at the indicated temperatures. Lines are the corresponding calculated values at the indicated temperatures respectively.

to compare with the calculated values. Usually, the experimental $S_{cc}(0)$ is obtained from Darken's excess stability functions [18]. In the absence of excess stability values, the values of $S_{cc}(0)$ are obtained from measured activity values through the relation

$$S_{cc}(0) = \frac{(1-c)a_{Zn}}{(\partial a_{Zn}/\partial c)_{T,P}} \tag{13}$$

Here, the experimental activity data were fitted to higher-order polynomials. Their derivatives were obtained and used in the above expression to obtain the required values of $S_{cc}(0)$.

Figure 3 shows the comparison of the calculated $S_{cc}(0)$ with the experimental ones for the three temperatures under investigation. In–Zn liquid alloy showed segregating

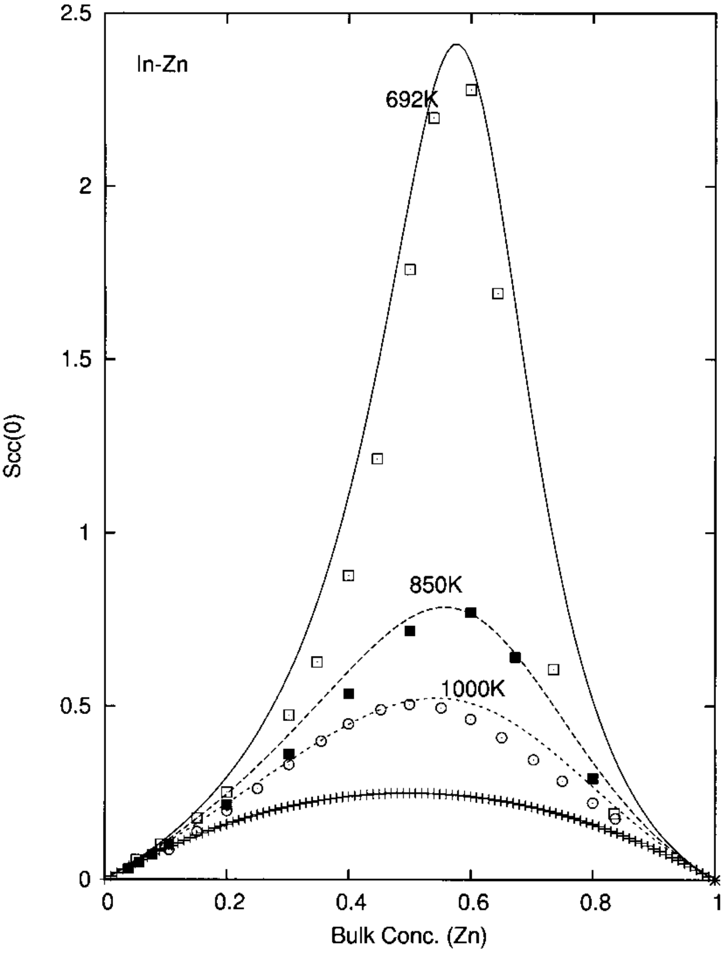

Figure 3. Bulk $S_{cc}(0)$ *vs.* bulk atomic fraction of Zn for In–Zn liquid alloy. Points rep. experimental values at the indicated temperatures. Lines are the corresponding calculated values at the indicated temperatures respectively. (+++) rep. ideal values of bulk $S_{cc}(0)$.

tendencies at all the temperatures, albeit at varying degrees. It should be noticed that there is a relatively large reduction in the peak value of $S_{cc}(0)$ as the temperature increased from 692 K to 850 K, a temperature difference of 158 K. As the temperature increased from 850 K to 1000 K, a temperature difference of 150 K, the observed reduction in the peak value of $S_{cc}(0)$ is comparatively small. This trend in the reduction of the peak value of $S_{cc}(0)$ suggests some form of exponential reduction in the strength of the segregation in this alloy as the temperature increases. This trend also suggests that with a further increase in the temperature, the $S_{cc}(0)$ of the alloy may approach ideal values. The reduction in the strength of segregation could be associated with the dissociation of the segregating clusters of the liquid alloy components. This dissociation occurs due to an increase in the temperature of the liquid alloy. The parameters in table 1 show that the ratio of the number of atoms in the segregating clusters remain constant throughout the temperatures of investigation. This suggests that the clusters of both, In and Zn atoms dissociate at the same rate as the temperature of the alloy increases. In this case, we refer to the In–Zn liquid alloy as a simple segregating liquid binary alloy.

From the expressions in equations (9) and (10), the surface compositions and the surface tension of In–Zn liquid alloy were numerically computed. The activity coefficients for the In and Zn atoms at the temperatures of investigation were computed from the expressions in equations (3) and (4), using the energy parameters given in table 1. The surface coordination fractions, p and q are taken as those for the close-packed structures with $p = 0.5$ and $q = 0.25$ for all the systems considered. The surface tension (σ_i) and atomic volume (Ω_i) at the melting temperature of the components of the alloy systems were taken from Ref. [19] (where i denotes the components In or Zn of the alloy). However, to obtain the surface tension and atomic volume at the working temperature of 692, 850, and 1000 K, the relationship between the temperature dependence of surface tension and atomic volume as given in Ref. [20] was used and is given as,

$$\sigma_i = \sigma_{im} + (T - T_{\mathrm{m}}) \frac{\partial \sigma_i}{\partial T} \tag{14}$$

and

$$\Omega_i = \Omega_{im}[1 + \theta(T - T_{\mathrm{m}})] \tag{15}$$

where, θ is the thermal coefficient of expansion, Ω_{im}, σ_{im} are the atomic volumes and the surface tension of the alloy components at their melting temperature T_{m}, and T is the working temperature in kelvins. The values of $\partial \sigma_i / \partial T$ and θ for the pure components of the alloy are obtained from Ref. [19]. The atomic surface area α_i for each atomic species of the different alloy systems was calculated following the relation [21] as:

$$\alpha_i = 1.102 \left(\frac{\Omega_i}{N} \right)^{2/3} \tag{16}$$

and the mean surface area α is then given as

$$\alpha = \sum_i c_i \alpha_i \tag{17}$$

where N is Avogadro's number and c_i are the concentrations of the alloy components.

The variation in the surface concentration of Zn against its bulk concentration for the three temperatures are shown in figure 4. The Zn segregates into the bulk of the alloy, while In segregates to the surface. This has far-reaching implications, when considering the wettability of the substrate and hence, the reliability of the solder joint by a multi-component solder involving In–Zn. However, we can infer from the figure that the segregation of In to the surface will decrease with an increase in temperature.

In figure 5, the calculated surface tension for the In–Zn alloy at different temperatures are presented. We have no experimental values to compare with our calculated

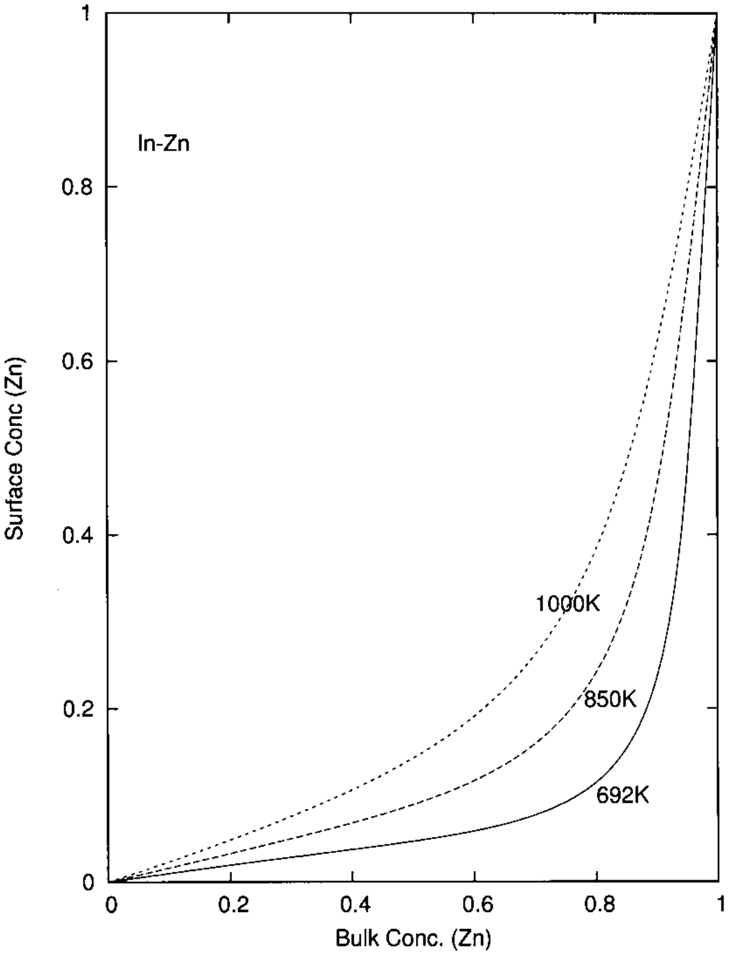

Figure 4. Surface concentration of Zn *vs.* Bulk concentration of Zn for In–Zn liquid alloy at 692 K, 850 K and 1000 K.

results, but calculations using this model had shown a reasonable agreement with the measured values [2]. In this figure, it is observed that the surface tension of the alloy decreases with an increase in temperature, below 0.55 bulk atomic fraction of Zn. A similar trend is also observed above the 0.9 bulk atomic fraction of Zn. However, between 0.55 and 0.9 bulk atomic fraction of Zn, there seems to be a reversal in the trend. The surface tension values in this region increases with an increase in the temperature. This increase in the surface tension of the alloy with an increase in temperature within this concentration range can be related to the observed relatively large increment in the surface concentration of Zn as the temperature is increased about the mentioned concentration range (figure 4).

The values of surface $S_{cc}(0)$ at the three different temperatures are presented in figure 6. The peak value for the ideal values of surface $S_{cc}(0)$ is 0.25. From the figure, the peak values of the calculated $S_{cc}(0)$ at the three temperatures of 692, 850 and 1000 K are all greater than 0.25. This indicates that at the surface of the alloy,

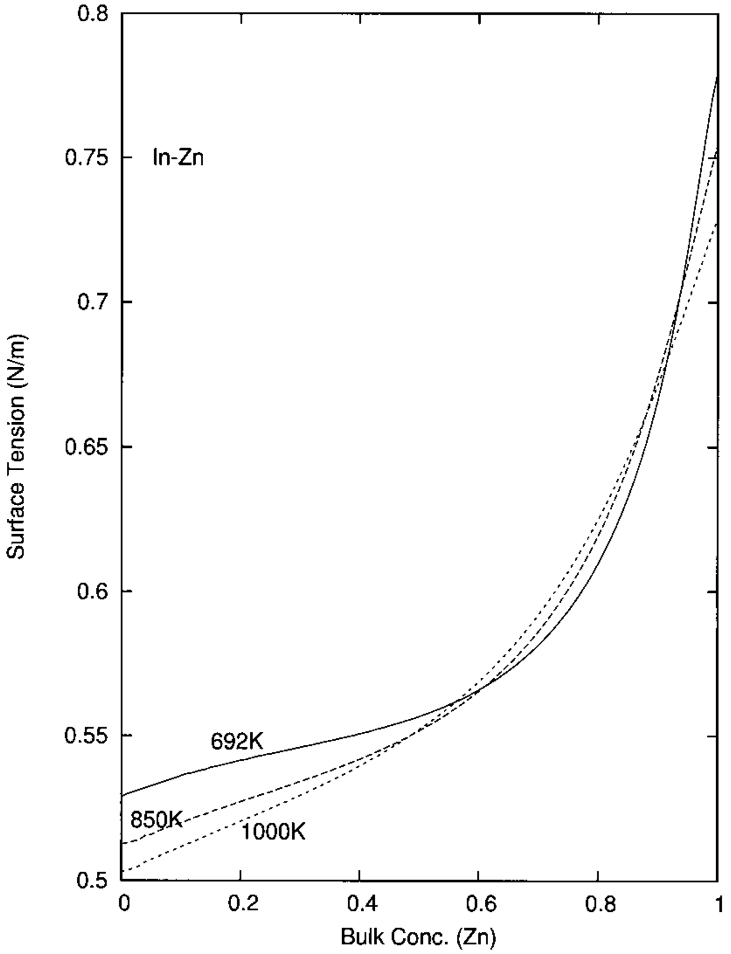

Figure 5. Surface tension *vs.* bulk concentration of Zn for In–Zn liquid alloy at 692 K, 850 K and 1000 K.

the components still exhibit a preference for like-atom pairs. This preference decreases with an increase in temperature as could be inferred from the peak values in the figure. In addition, the peak value of the surface $S_{cc}(0)$ does not appear to decrease exponentially as that observed in the bulk; hence we can say that the strength of the segregation at the surface decreases proportionately with an increase in temperature. As in the bulk, segregation at the surface of this alloy is strongest at low liquid alloy temperatures. The segregation of Zn atoms to the surface is pronounced only for alloys with very high Zn content.

4. Conclusion

In–Zn is a strong phase-segregating liquid binary alloy. The phase-segregating tendencies in the bulk appear to decrease exponentially with an increase in temperature.

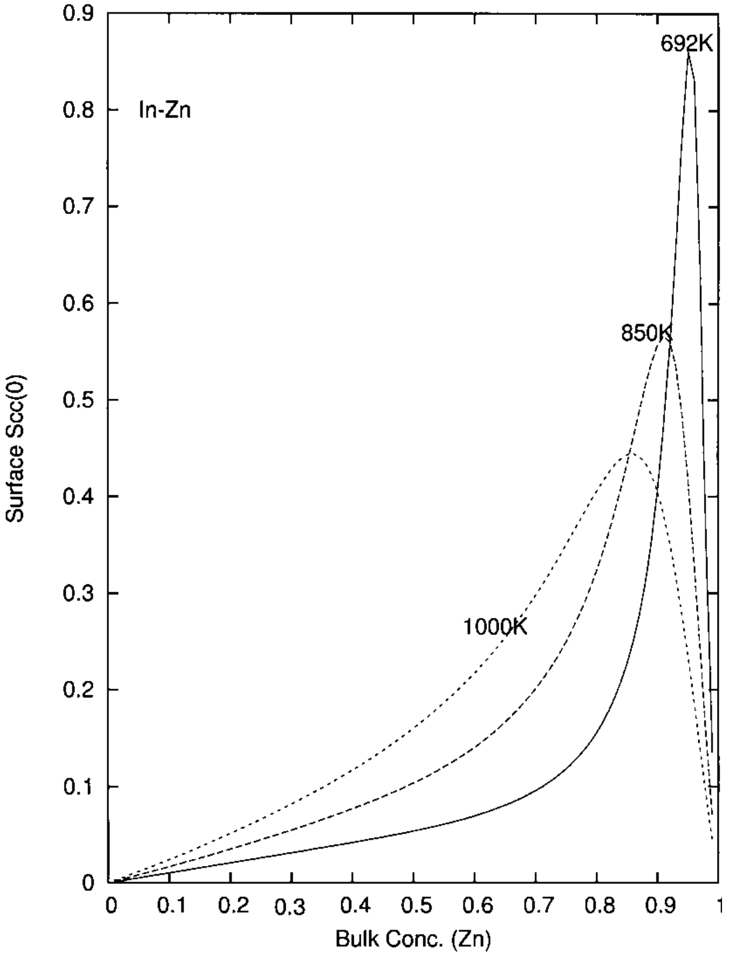

Figure 6. Surface $S_{cc}(0)$ *vs*. Bulk Concentration of Zn for In–Zn liquid alloy at 692 K, 850 K and 1000 K.

The alloy shows phase-segregating tendencies at the surface. The strength of the segregation also decreases with the increase in temperature but not in the same rate as in the bulk. The surface tension values for In–Zn increases with increase in temperature, between 0.55 and 0.9 bulk atomic fraction of Zn. The response of the properties of In–Zn to temperature is not complex, hence the alloy can be referred to as a simple segregating liquid alloy.

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