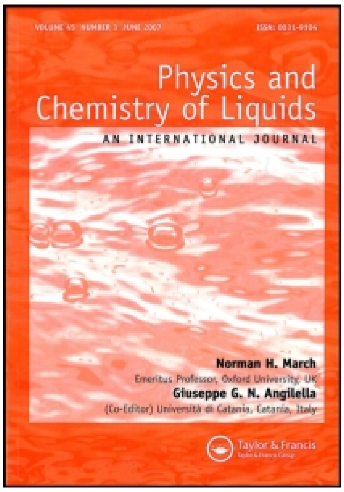

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Correlation between bulk and surface properties of ternary Ag-Sn-Zn liquid alloys and concerned binaries

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Correlation between bulk and surface properties of ternary Ag–Sn–Zn liquid alloys and concerned binaries

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A correlative study of the bulk and surface properties of the ternary Ag–Sn–Zn liquid alloys has been undertaken by extending the descriptions of concerned binaries (Ag–Sn, Sn–Zn, and Ag–Zn), obtained from statistical mechanical theory in the frame-work of quassi-lattice approximations. An improved model, in which the selection of binary compositions involves the correlation of one particular component with other components of the ternary system, has been used to compute the free energy of mixing of Ag–Sn–Zn system. The concentration dependence of the surface tension and surface composition has been explained by obtaining expression for the activity coefficients and extending the surface description of binary systems. It is worth mentioning that same set of interaction energies as those used for the bulk and surface calculations of the concerned binaries has been used to investigate the concentration dependence of free energy of mixing, surface tension (σ) and surface composition of the ternary system. The theoretical investigation of binary systems suggest the presence of short range order in Ag–Sn and Ag–Zn systems leading to the formation of intermetallic compounds (Ag_3Sn in Ag–Sn and AgZn in Ag–Zn) in the melt. Sn–Zn system is characterized by the existence of diatomic tin in the melt. The concentration dependence of the free energy of mixing of Ag–Sn–Zn system for three cross section ($Ag:Sn=1:1$, $1:3$ and $3:1$) has been clearly explained by our theoretical model. There is slight decrease in σ for $Ag:Sn=1:1$ up to $x_{Zn}\approx 0.4$ whereas sharp decrease up to 50% Zn is observed in case of $Ag:Sn=3:1$. The σ for $Ag:Sn=1:3$ remains almost constant up to $x_{Zn}\approx 0.25$. The surfaces of Ag–Sn–Zn system for all three cross section ($Ag:Sn=1:1$, $1:3$ and $3:1$) are quite enriched with Sn-atoms. The degree of segregation is lowest in $Ag:Sn=3:1$.

Keywords: Ag–Sn–Zn liquid alloys; Surface tension; Surface segregation; Geometrical models; Sn-based liquid alloys

1. Introduction

Owing to experimental complexities, the data for the thermodynamic and structural properties of multicomponent systems is very scarce. In view of these limitations, attempts [1–4] are being made to understand the alloying behavior in such systems by using theoretical models. A theoretical approach not only helps in describing the anomalous mixing behavior of multicomponent systems, but also generates data.

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All the geometrical models [5–9] used for the calculation, which are based on the different modes of selection of binary compositions are extension of mixing properties of concerned binaries with assigned probability weight, but all these models suffer with some limitations [2]. Some models do not reduce to limiting form in case of two components being similar. On the other hand, many models require human interference in fixing the edges of the polyhedron by suitable element. So no model can be regarded as complete and universal from an applicability point of view. Keeping these limitations in mind, an attempt has been made to improve the model by incorporating the correlation of one component with all other components of the multi-component system in the selection of binary compositions. It is observed that this approach not only overcomes the problems discussed before but also gives better results. Though some progress in the field of bulk properties [1–5] has been made in recent years, the understanding of the surface phenomenon in these systems is still rather unexplored. In order to have clear picture of multi-component systems, one requires to undertake the theoretical investigation of bulk as well as surface properties by extending the descriptions of concerned binaries through an improved geometrical model and establish a correlation between them. In recent years, emphasis is being laid to investigate Sn-based alloys so as to find a suitable substitute [9–15] for conventional solder alloys, $Sn_{0.6}Pb_{0.4}$, since it became known that lead has hazardous effect and environmental concerns. Of all non-lead systems, the melting temperature of Sn–Zn system [16] is very close to the eutectic temperature of Sn–Pb. But Zn is well known for the problems related to wettability and corrosion and very liable to oxidation. On the other hand, Ag–Sn system [17,18], though having higher melting temperature exhibits chemical short range order. With the view to investigate the effect of zinc on the alloying behavior of Ag–Sn system and overall change in the properties of Sn–Zn system, we have chosen Ag–Sn–Zn system for the investigation.

The grand partition function for the binary systems has been solved [18,19] in the framework of quassi-lattice approximations [20–22] to obtain expressions for thermodynamic functions and surface tension for different types of binary liquid alloys. The expressions have been used to investigate the bulk and surface properties of binary systems. The descriptions of binary systems have been extended [3,23] to Ag–Sn–Zn liquid alloys to investigate the bulk and surface properties.

Theoretical formalism for different types of binaries has been presented in section 2, while section 3 deals with the ternary system. Results and discussion has been given in section 4 and we have concluded in section 5.

2. Theoretical formalism for binary liquid alloys

2.1. *Free energy of mixing and activity coefficient*

Various expressions for free energy of mixing and activity coefficients for binary liquid alloys may be obtained by solving the grand partition function in the framework of quassi-lattice approximations.

2.1.1. Compound formation (CF) model. In compound formation (CF) model [18–20], it is assumed that component elements A and B of the binary alloy A–B might arrange preferentially to form chemical complexes, $A_\mu B_\nu(\mu A + \nu B \leftrightharpoons A_\mu B_\nu$; μ and ν are small integers) in the liquid state. The solution of the grand partition function is based on the assumption [20] that the energy of a given nearest neighbour bond in case of compound formation will be different from that of regular solution. If ε_{ij} is the energy of *i–j* bond for regular solution then the energy in case of compound formation will be $\varepsilon_{ij} + P_{ij}\Delta\varepsilon_{ij}$. $\Delta\varepsilon_{ij}$ is the measure of the difference of the energy of *i–j* bond when one of the bond forming components (*i* or *j*) is a part of complex, $A_\mu B_\nu$. P_{ij} denotes the probability of finding *i–j* bond as a part of complex.

After doing some algebra, one obtains an expression for the ratio of activity coefficients, γ ($=\gamma_A/\gamma_B$ where γ_A and γ_B are activity coefficients of component A and B, respectively) in terms of concentration, C of the component A as

$$\ln\gamma = \frac{1}{2}Z\ln\left\{\frac{(1-C)(\beta+2C-1)}{C(\beta-2C+1)}\right\} + \frac{1}{2}K_B T(P_{AA}\Delta w_{AA} - P_{BB}\Delta w_{BB}) + I \tag{1}$$

Z is the coordination number and I is a constant independent of concentration but may depend upon temperature and pressure. It is determined by solving $\int_0^1 \ln\gamma\, \mathrm{d}C = 0$. K_B and T refer to Boltzman's constant and absolute temperature, respectively. Δw_{ij} ($=Z\Delta\varepsilon_{ij}$) is the additional interaction energy terms in CF model. The probability P_{ij} is given as

$$P_{AB} = C^{\mu-1}(1-C)^{\nu-1}\left[2 - C^{\mu-1}(1-C)^{\nu-1}\right] \tag{2a}$$

$$P_{AA} = C^{\mu-2}(1-C)^{\nu}\left[2 - C^{\mu-2}(1-C)^{\nu}\right]; \quad \mu \geq 2 \tag{2b}$$

$$P_{AB} = C^{\mu}(1-C)^{\nu-2}\left[2 - C^{\mu}(1-C)^{\nu-2}\right]; \quad \nu \geq 2 \tag{2c}$$

β has been set as

$$\beta = [1 + 4C(1-C)(\eta^2 - 1)]^{1/2} \tag{3}$$

with

$$\eta = \frac{(\rho_{AA}\rho_{BB})^{1/2}}{\rho_{AB}} \tag{4}$$

ρ_{ij} stands for

$$\rho_{ij} = \exp\left[\frac{-(\varepsilon_{ij} + P_{ij}\Delta\varepsilon_{ij})}{K_B T}\right] \tag{5}$$

Equations (4) and (5) give η as

$$\eta^2 = \exp\left[\frac{2w}{ZK_B T}\right]\exp\left[\frac{2P_{AB}\Delta\varepsilon_{AB} - P_{AA}\Delta\varepsilon_{AA} - P_{BB}\Delta\varepsilon_{BB}}{K_B T}\right] \tag{6}$$

where w, generally termed as order energy in regular solution theory is given as $Z(\varepsilon_{AB} - (1/2)\varepsilon_{AA} - (1/2)\varepsilon_{BB})$.

On using standard thermodynamic relation between γ and excess free energy of mixing, $G_{\mathrm{M}}^{\mathrm{xs}}(=(G_{\mathrm{M}}-G_{\mathrm{M}}^{\mathrm{id}})$; G_{M} is the free energy of mixing and $G_{\mathrm{M}}^{\mathrm{id}}$ denotes ideal free energy of mixing),

$$G_{\mathrm{M}}^{\mathrm{xs}} = NK_{\mathrm{B}}T\int_0^C \ln\gamma \tag{7}$$

one obtains analytical expressions for $G_{\mathrm{M}}^{\mathrm{xs}}$ and activity coefficients (γ_{A} and γ_{B}) as

$$G_{\mathrm{M}}^{\mathrm{xs}} = N[w\varphi + \Delta w_{\mathrm{AB}}\varphi_{\mathrm{AB}} + \Delta w_{\mathrm{AA}}\varphi_{AA} + \Delta w_{\mathrm{BB}}\varphi_{\mathrm{BB}}] \tag{8}$$

$$K_{\mathrm{B}}T\ln\gamma_{\mathrm{A}} = w\theta + \Delta w_{\mathrm{AB}}\theta_{\mathrm{AB}} + \Delta w_{\mathrm{AA}}\theta_{AA} + \Delta w_{\mathrm{BB}}\theta_{\mathrm{BB}} \tag{9a}$$

$$K_{\mathrm{B}}T\ln\gamma_{\mathrm{B}} = wg + \Delta w_{\mathrm{AB}}g_{\mathrm{AB}} + \Delta w_{\mathrm{AA}}g_{AA} + \Delta w_{\mathrm{BB}}g_{\mathrm{BB}} \tag{9b}$$

φ_{ij}, θ_{ij} and g_{ij} are functions of concentration and depend upon the set of μ and ν.

For $\mu = 3$ and $\nu = 1$, these are

$$\varphi = C(1-C) \tag{10a}$$

$$\varphi_{\mathrm{AB}} = \frac{1}{5}C + \frac{2}{3}C^3 - C^4 - \frac{1}{5}C^5 + \frac{1}{3}C^6 \tag{10b}$$

$$\varphi_{\mathrm{AA}} = -\frac{3}{20}C + \frac{2}{5}C^3 - \frac{3}{4}C^4 + \frac{2}{5}C^5 - \frac{1}{6}C^6 \tag{10c}$$

$$\boldsymbol{\phi}_{\mathbf{BB}} = 0 \tag{10d}$$

$$\theta = (1-C)^2 \tag{11a}$$

$$\theta_{\mathrm{AB}} = \frac{1}{5} + 2C^2 - \frac{16}{3}C^3 + 2C^4 - \frac{14}{5}C^5 - \frac{5}{3}C^6 \tag{11b}$$

$$\theta_{\mathrm{AA}} = -\frac{3}{20} + 2C^2 - \frac{13}{3}C^3 + \frac{17}{4}C^4 - \frac{13}{5}C^5 + \frac{5}{6}C^6 \tag{11c}$$

$$\theta_{\mathrm{BB}} = 0 \tag{11d}$$

$$g = C^2 \tag{12a}$$

$$g_{\mathrm{AB}} = -\frac{4}{3}C^3 + 3C^4 + \frac{4}{5}C^5 - \frac{5}{3}C^6 \tag{12b}$$

$$g_{\mathrm{AA}} = -\frac{4}{3}C^3 + \frac{9}{4}C^4 - \frac{8}{5}C^5 + \frac{5}{6}C^6 \tag{12c}$$

$$g_{\mathrm{BB}} = 0 \tag{12d}$$

If likely chemical complexes to be formed are of AB type ($\mu = \nu = 1$) then equation (2) gives $P_{\mathrm{AB}} = 1$ and $P_{\mathrm{AA}} = P_{\mathrm{BB}} = 0$ and equation (6) for η^2 becomes

$$\eta^2 = \exp\left[\frac{2(w + Z\Delta\varepsilon_{\mathrm{AB}})}{ZK_{\mathrm{B}}T}\right] \tag{13}$$

and $\ln\gamma$ (equation (1)) becomes

$$\ln\gamma = \left(\frac{Z}{2}\right)\ln\left\{\frac{(1-C)(\beta+2C-1)}{C(\beta-2C+1)}\right\} \tag{14}$$

Generally, $\mathrm{G}_{\mathrm{M}}^{\mathrm{xs}}$ and activity coefficients (γ_{A} and γ_{B}) for such type of alloys are expressed as

$$\mathrm{G}_{\mathrm{M}}^{\mathrm{xs}} = \frac{Z}{2}NK_{\mathrm{B}}T[C\ln\gamma_{\mathrm{A}} + (1-C)\ln\gamma_{\mathrm{B}}] \tag{15}$$

with

$$\ln\gamma_{\mathrm{A}} = \frac{Z}{2}\ln\left\{\frac{\beta+2C-1}{C(\beta+1)}\right\} \tag{16a}$$

$$\ln\gamma_{\mathrm{B}} = \frac{Z}{2}\ln\left\{\frac{\beta-2C+1}{(1-C)(\beta+1)}\right\} \tag{16b}$$

It will be proper to mention that in case of no compound formation, i.e. regular solution, all probability terms and $\Delta\varepsilon_{ij}$ become zero. Equations (15) and (16) remain same but η^2 becomes $\exp[2w/ZK_{\mathrm{B}}T]$. This corresponds to regular solution theory.

2.1.2. Self-associating (SA) mixtures. Demixing behavior of many binary liquid alloys which do not exhibit size mismatch effect can be explained by assuming that polyatomic clusters [22] ($i\mathrm{A} \leftrightharpoons \mathrm{A}_i, j\mathrm{B} \leftrightharpoons \mathrm{B}_j$; i and j being the number of atoms in the cluster of A and B type matrix, respectively) might exist in the melt. Existence of polyatomic clusters is due to self-association of component atoms. For such type of SA mixtures, $G_{\mathrm{M}}^{\mathrm{xs}}$ and γ_i are given as

$$G_{\mathrm{M}}^{\mathrm{xs}} = NK_{\mathrm{B}}T\left[C\ln\frac{\phi}{C} + (1-C)\left\{\ln\frac{1-\phi}{1-C}\right\} + \frac{\phi(1-\phi)(j+C(i-j))w}{K_{\mathrm{B}}T}\right] \tag{17}$$

$$\ln\gamma_{\mathrm{A}} = 1 + \ln(\phi/C) - (\phi/C) + \frac{(1-\phi)^2 iw}{K_{\mathrm{B}}T} \tag{18a}$$

$$\ln\gamma_{\mathrm{B}} = \ln\left\{\frac{1-\phi}{1-C}\right\} + \frac{\phi(i-j)}{i} + \frac{\phi^2 jw}{K_{\mathrm{B}}T} \tag{18b}$$

with

$$\phi = \frac{iC}{(j + C(i - j))} \tag{19}$$

w is the order energy.

2.2. *Surface tension and surface composition*

A general expression for the surface tension of binary liquid alloys may be obtained by constructing a grand partition function [18,21] for the surface and solving it in the framework of quassi-lattice approximations. These are given as

$$\sigma = \sigma_A + (K_B T/\alpha)\ln(C^s/C) + (K_B T/\alpha)\ln(\gamma_A^S/\gamma_A) \tag{20a}$$

$$= \sigma_B + (K_B T/\alpha)\ln((1 - C^s)/(1 - C)) + (K_B T/\alpha)\ln(\gamma_B^s/\gamma_B) \tag{20b}$$

where σ_i ($i = $A, B) is the surface tension of pure components and α is mean atomic surface area. C^s and γ_i^s ($i = $A or B) refer to the surface concentration of component A and activity coefficient of ith component at the surface, respectively. Various expressions for σ may be obtained for different types of alloys if one has proper analytical expressions for γ_i and γ_i^s.

In view of the absence of analytical expression for γ_i^s, it is assumed that it is related with γ_i through the relation

$$\ln\gamma_i^s = p\ln\gamma_i^* + q\ln\gamma_i \tag{21}$$

where $\ln\gamma_i^* \to \ln\gamma_i$ containing C^s in place of C. p and q, usually termed as surface coordination fractions, are fractions of total number of nearest neighbours made by an atom within the layer in which it lies and in the adjoining layers, respectively, so that $p + 2q = 1$. For closed packed structure, one has $p = 1/2$ and $q = 1/4$.

2.2.1. CF alloys. On using equations (9), (11) and (12) in equation (20) in conjunction with equation (21), we get an expression for the surface tension for CF alloys, for $\mu = 3$ and $\nu = 1$ as

$$\begin{aligned}\sigma = \sigma_A + (K_B T/\alpha)\big[&\ln(C^s/C) + (w/K_B T)\{p(\theta^s - \theta) - q\theta\}\\ &+ (\Delta w_{AB}/K_B T)\{p(\theta_{AB}^s - \theta_{AB}) - q\theta_{AB}\} + (\Delta w_{AA}/K_B T)\{p(\theta_{AA}^S - \theta_{AA}) - q\theta_{AA}\}\big]\end{aligned} \tag{22a}$$

$$\begin{aligned}= \sigma_B + (K_B T/\alpha)\big[&\ln\{(1 - C^s)/(1 - C)\} + (w/K_B T)\{p(g^s - g) - qg\}\\ &+ (\Delta w_{AB}/K_B T)\{p(g_{AB}^S - g_{AB}) - qg_{AB}\} + (\Delta w_{AA}/K_B T)\{p(g_{AA}^S - g_{AA}) - qg_{AA}\}\big]\end{aligned} \tag{22b}$$

where θ, θ_{ij}, g and g_{ij} are given by equations (11) and (12). θ^s, θ_{ij}^s, g^s and g_{ij}^s are functions of surface concentration C^s with the same form as that of equations (11) and (12).

Application of equation (16) in equation (20) in conjunction with equation (21) give expression for the surface tension for $\mu = 1$ and $\nu = 1$,

$$\sigma = \sigma_A + (K_B T/\alpha)\ln(C^s/C) + (ZK_B T/2\alpha)\big[p\ln\big\{(\beta^s + 1 - 2C^s)/(C^s(1+\beta^s))\big\} + (q-1)\ln\big\{(\beta + 1 - 2C)/(C(1+\beta))\big\}\big] \tag{23a}$$

$$= \sigma_B + (K_B T/\alpha)\ln(1 - C^s)/(1 - C) + (ZK_B T/2\alpha)\big[p\ln\big\{(\beta^s - 1 + 2C^s)/((1 - C^s)(1+\beta^s))\big\} + (q-1)\ln\big\{(\beta - 1 + 2C)/((1 - C)(1+\beta))\big\}\big] \tag{23b}$$

β is already defined by equation (3) whereas β^s is given by

$$\beta^s = \big[1 + 4C^s(1 - C^s)(\eta^2 - 1)\big]^{1/2} \tag{24}$$

η in this case is given by equation (13).

2.2.2. SA alloys. Equations (18), (20) and (21) give σ for self-associating mixtures as

$$\sigma = \sigma_A + (K_B T/\alpha)\big[\ln(C^s/C) + p\big\{\ln(C\phi^s/C^s\phi) + (\phi C^s - \phi^s C)/CC^s\big\} + q\{\ln(C/\phi) + (\phi - C)/C\} + (iw/K_B T)\big\{p(1-\phi^s)^2 + (q-1)(1-\phi)^2\big\}\big] \tag{25a}$$

$$= \sigma_B + (K_B T/\alpha)\big[\ln\{(1 - C^s)/(1 - C)\} + p\{\ln((1-C)(1-\phi^s)/(1-C^s)(1-\phi)) + (i-j)(\phi^s - \phi)/i\} - q\{\ln\{(1-\phi)/(1-C)\} + \phi(i-j)/i\} + (jw/K_B T)\big\{p\phi^{s2} + (q-1)\phi^2\big\}\big] \tag{25b}$$

ϕ is already defined by equation (19). ϕ^s is expressed in terms of C^s in equation (19).

3. Geometrical model for ternary system

It is clear from the literature [2,5–9] that all geometrical models for the multicomponent systems are based on the assumption that thermodynamic properties of mixing can be expressed as a combination of concerned binaries with an assigned probability weight, i.e.

$$\Delta G^{xs} = \sum_{ij} W_{ij} G_{ij}^{xs} \tag{26}$$

where ΔG^{xs} and G_{ij}^{xs} are excess free energy of mixing of the multicomponent system and binary *i*–*j* respectively. W_{ij} refers to assigned probability weight, given as

$$W_{ij} = \frac{x_i x_j}{X_{i(i,j)} X_{j(i,j)}} \tag{27}$$

where x_i and x_j are compositions of i and jth component of multicomponent systems. $X_{i(i,j)}$ is the composition of ith component in binary system i–j. $X_{i(i,j)}$ is generally expressed as

$$X_{i(i,j)} = \left(\frac{1 + x_i - x_j}{2}\right) - \delta_{ij} \tag{28}$$

δ_{ij} is a parameter. Different existing models are characterized by different values for δ_{ij}. For example, $\delta_{ij} = 0$ refers to Moggiannu model [6]. When $\delta_{ij} = (x_i - x_j)(1 - x_i - x_j)/2(x_i + x_j)$, the model corresponds to Kohler's model [5].

3.1. *Free energy of mixing*

In Kohler's model [5], excess free energy of mixing, ΔG^{xs} of the ternary system is expressed as

$$\Delta G^{\mathrm{xs}} = (x_1 + x_2)^2 G_{12}^{\mathrm{xs}} + (x_2 + x_3)^2 G_{23}^{\mathrm{xs}} + (x_3 + x_1)^2 G_{31}^{\mathrm{xs}} \tag{29}$$

As discussed in detail in section 1, no existing model can be regarded as complete model from an applicability point of view. An improved model [1] that incorporates the impact of other components (k) of the ternary system on the selection of binary composition, gives

$$X_{i(i,j)} = x_i + x_k \xi_{ij} \tag{30}$$

ξ_{ij} is similarity coefficient between the components (i and j) of the binary i–j and expressed through a correlative term, $\eta_{i(ij,\,ik)}$ as

$$\xi_{ij} = \frac{\eta_{i(ij,ik)}}{\eta_{i(ij,ik)} + \eta_{j(ji,jk)}} \tag{31}$$

The correlation of ith component with other components (j and k) of the ternary system is described by $\eta_{i(ij,\,ik)}$. It is expressed in terms of excess free energy of mixing of two binaries, i.e. i, j and i, k by using deviation square sum rule.

$$\eta_{i(ij,ik)} = \int_{X_i=0}^{X_i=1} (G_{ij}^{\mathrm{xs}} - G_{ik}^{\mathrm{xs}})^2 \mathrm{d}X_i \tag{32}$$

where X_i is the binary composition of ith component in two binaries, i.e. ij and ik. The similarity of two components of the ternary system can be easily understood from the magnitude of correlative term, $\eta_{i(ij,\,ik)}$.

For j being similar to kth component

$$\eta_{i(ij,ik)} \to 0 \quad \text{otherwise } \eta_{i(ij,ik)} > 0 \text{ and } \xi_{ij} = 0.$$

For kth component being similar to ith component

$$\eta_{j(ji,jk)} \to 0 \quad \text{otherwise } \eta_{j(ji,jk)} > 0 \text{ and } \xi_{ij} = 1.$$

A small value of ξ_{ij} indicates the similarity of k and jth components while large value refers to the similarity of i and kth components.

Application of binary expressions for G_{ij}^{xs} for $Z=10$ [equations (8), (15) and (17)] in equation (32) give correlative terms as

$$\begin{aligned}\eta_{1(12,13)} = \int_{X_1=0}^{X_1=1} & N^2K_{\mathrm{B}}^2T^2\big[\big\{(w_{12}/K_{\mathrm{B}}T)X_1(1-X_1)\\ & +(\Delta w_{12}/K_{\mathrm{B}}T)((1/5)X_1+(2/3)X_1^3-X_1^4-(1/5)X_1^5+(1/3)X_1^6)\big\}\\ & -(Z/2)\big\{X_1\ln\{(\beta_{13}-1+2X_1)(1-X_1)/(X_1(\beta_{13}+1-2X_1))\}\\ & +\ln\big\{(\beta_{13}+1-2X_1)/((1-X_1)(1+\beta_{13}))\big\}\big\}\big]^2\,\mathrm{d}X_1\end{aligned}\tag{33a}$$

$$\begin{aligned}\eta_{2(21,23)} = \int_{X_2=0}^{X_2=1} & N^2K_{\mathrm{B}}^2T^2\big[\big\{(w_{12}/K_{\mathrm{B}}T)X_2(1-X_2)\\ & +(\Delta w_{12}/K_{\mathrm{B}}T)((4/5)X_2-X_2^2-(4/3)X_2^3+3X_2^4-(9/5)X_2^5+(1/3)X_2^6)\big\}\\ & -\big\{X_2\ln i+\big\{(1-X_2)\ln j-\ln(j+(i-j)X_2)\\ & +ijX_2(1-X_2)(w_{23}/K_{\mathrm{B}}T)/(j+(i-j)X_2)\big\}\big]^2\,\mathrm{d}X_2\end{aligned}\tag{33b}$$

$$\begin{aligned}\eta_{3(31,32)} = \int_{X_3=0}^{X_3=1} & N^2K_{\mathrm{B}}^2T^2\big[(Z/2)\big\{X_3\ln\big\{(\beta_{31}-1+2X_3)(1-X_3)/(X_3(\beta_{31}+1-2X_3))\big\}\\ & +\ln\big\{(\beta_{31}+1-2X_3)/((1-X_3)(1+\beta_{31}))\big\}\big\}\\ & -\big\{(1-X_3)\ln i+X_3\ln j-\ln(i-X_3(i-j))\\ & +ijX_3(1-X_3)(w_{23}/K_{\mathrm{B}}T)/(i-X_3(i-j)))\big\}\big]^2\,\mathrm{d}X_3\end{aligned}\tag{33c}$$

$G_{\mathrm{M}}^{\mathrm{xs}}$ for SA mixtures [equation (17)] has been transformed in terms of i and j which are already defined. β_{ij} appearing in above equations refer to i–j binary and is given by equation (3).

The concentration terms C (concentration of ith component of binary i–j) have been replaced by X_1, X_2 and X_3. Above equations for $\eta_{i(ij,\,ik)}$ can be used to calculate the values of similarity coefficients (ξ_{12}, ξ_{23} and ξ_{31}) for the ternary system through equation (31).

One may get an expression for excess free energy of mixing, ΔG^{xs} for the ternary system by using binary expressions for $G_{\mathrm{M}}^{\mathrm{xs}}$ [equations (8), (15) and (17)] in equations (26), (27) and (30). This is given as

$$\begin{aligned}\Delta G^{\mathrm{xs}} = NK_{\mathrm{B}}T[&(x_1x_2/f(1-f))\{w_{12}f(1-f)+\Delta w_{12}f_1\}\\ & +(x_2x_3/f_2(1-f_2))\{f_2\ln(2/(1+f_2))-(1-f_2)\ln(1+f_2)+2f_2(1-f_2)w_{23}/(1+f_2)\}\\ & +(x_3x_1/f_3(1-f_3))(Z/2)\{f_3\ln(f_4(1-f_3)+1)+(1-f_3)\ln(f_3f_4+1)\\ & -\ln(f_3f_4(1-f_3)+1)\}]\end{aligned}\tag{34}$$

where

$$\left.\begin{aligned}
f &= x_1 + x_3\xi_{23}\\
f_1 &= (1/5)f + (2/3)f^3 - f^4 - (1/5)f^5 + (1/3)f^6\\
f_2 &= x_2 + x_1\xi_{12}\\
f_3 &= x_3 + x_2\xi_{31}\\
f_4 &= K(1 - Kf_3(1 - f_3))\\
&\text{with}\\
K &= \exp[(2w_{31}/ZK_\mathrm{B}T) - 1]
\end{aligned}\right| \tag{35}$$

w_{12} and Δw_{12} are interaction energy parameters for CF binary alloys for 3 : 1 type ($\mu = 3$ and $\nu = 1$) compounds in the melt. w_{23} and w_{31} refer to order energies for SA and CF alloys for 1 : 1 type ($\mu = 1$ and $\nu = 1$) compounds, respectively.

The activity coefficients (γ_i) and ΔG^xs of the multicomponent systems are related through the relation [3,23]

$$RT\ln\gamma_i = \Delta G^\mathrm{xs} + \sum_{j=2}^{m}(\delta_{ij} - x_j)(\partial\Delta G^\mathrm{xs}/\partial x_j) \tag{36}$$

where δ_{ij} is Kronecker's symbol with the condition,

$$\delta_{ij} = 0 \text{ if } i \neq j \quad\text{and}\quad \delta_{ij} = 1 \text{ if } i = j.$$

For ternary system above relation reduces to

$$RT\ln\gamma_1 = \Delta G^\mathrm{xs} + x_2(\partial\Delta G^\mathrm{xs}/\partial x_2) - x_3(\partial\Delta G^\mathrm{xs}/\partial x_3) \tag{37}$$

$$RT\ln\gamma_2 = \Delta G^\mathrm{xs} + (1 - x_2)(\partial\Delta G^\mathrm{xs}/\partial x_2) - x_3(\partial\Delta G^\mathrm{xs}/\partial x_3) \tag{38}$$

$$RT\ln\gamma_3 = \Delta G^\mathrm{xs} - x_2(\partial\Delta G^\mathrm{xs}/\partial x_2) + (1 - x_3)(\partial\Delta G^\mathrm{xs}/\partial x_3) \tag{39}$$

On using equations (34), (37) and (39), one obtains analytical expressions for γ_i of ternary system. These are

$$\begin{aligned}
\ln\gamma_1 = {}& x_2w_{12}(1 - x_1) + x_2\Delta w_{12}\{(f_1/(f(1 - f)) - x_1P\}\\
&+ x_2x_3(\xi_{23} - 1)(\ln 2)/\big((1 - f_2)^2\big) + x_2x_3\{f_2(f_2 - 2\xi_{23}) + \xi_{23}\}\{\ln(1 + f_2)\}/\big(f_2^2(1 - f_2)^2\big)\\
&+ x_2x_3(f_2 - \xi_{23})/f_2(1 - f_2)^2 - 2x_2x_3w_{23}(1 + \xi_{23})/(1 + f_2)^2\\
&+ (Z/2)\big[f_3(P_4 - P_1P_2 - P_3) + x_2x_3(1 - \xi_{31})\{\ln(f_4(1 - f_3) + 1)\}/(1 - f_3)^2\\
&+ (x_3 - x_2(x_3 - x_2))\{\ln(f_3f_4 + 1)\}/f_3\\
&+ \big\{f_3(x_1x_3(1 + 2f_3) - (1 - f_3)\big(x_2^2 + x_3^2 - 2x_1x_3^2\big)\big\}\big(\ln\big\{f_3f_4(1 - f_3) + 1\big\}\big)/\big(f_3^2(1 - f_3)^2\big)\big]
\end{aligned} \tag{40}$$

$$\begin{aligned}\ln\gamma_2 = {} & x_1 w_{12}(1-x_2) + x_1\Delta w_{12}/((1-f))\{x_2 fP + f_{1x_3}(1-\xi_{12})/(f(1-f))\} \\ & + x_3(\ln\ 2)/(1-f_2) + x_3\bigl\{x_2(f_2^2 - x_2) - x_1\xi_{23}(1-x_1\xi_{23})\}\{\ln(1+f_2)\bigr\}/\bigl(f_2^2(1-f_2)^2\bigr) \\ & - x_2x_3/(f_2(1+f_2)) + 2x_3w_{23}(1-x_2+x_1\xi_{23})/(1+f_2)^2 \\ & + (Z/2)[(f_3-\xi_{31})(P_4-P_1P_2-P_3) + x_1x_3(1-\xi_{31})\{\ln(f_4(1-f_3)+1)\}/(1-f_3)^2 \\ & + \bigl\{f_3(1-x_2)(x_3-x_2) - x_1x_3\xi_{31}\bigr\}\bigl\{\ln(f_3f_4+1)\bigr\}/f_3^2 \\ & + \bigl\{x_1x_3(f_3-\xi_{31})(2f_3+1) + f_3(1-f_3)(x_2-x_2^2-x_3^2)\bigr\} \\ & \quad \times\bigl(\ln\{f_3f_4(1-f_3)-1\}\bigr)/\bigl(f_3^2(1-f_3)^2\bigr)] \end{aligned} \tag{41}$$

$$\begin{aligned}\ln\gamma_3 = {} & -x_1x_2w_{12} + (x_1x_2\Delta w_{12}/(1-f))\{P(f-\xi_{12}) + (f_1(\xi_{12}-1)/(f(1-f))\} \\ & + x_1x_2(1-\xi_{23})(\ln 2)/(1-f_2)^2 + x_2\{x_3f_2(f_2-\xi_{23}) + x_2(1-x_2)(2\xi_{23}-1) \\ & - x_1\xi_{23}(1-\xi_{23}(x_1+2x_3))\}\{\ln((1+f_2)\}/\bigl(f_2^2(1-f_2)^2\bigr) + x_2x_3/(1-f_2)^2 \\ & + 2x_3w_{23}(x_1+x_2+f_2)/(1+f_2)^2 + (Z/2)[(1-f_3)(P_1P_2+P_3-P_4) \\ & + x_1\{\ln(f_4(1-f_3)+1)\}/(1-f_3) + x_2\{x_1\xi_{31} - f_3(x_3-x_2)\}\{\ln(f_3f_4+1)\}/f_3^2 \\ & + \{x_1x_2\xi_{31})(1+2f_3) - (1-x_3)\{f_3(1-f_3(1-x_3) - x_1x_3(1-2f_3)\}\} \\ & \times\{\ln(f_3f_4(1-f_3)+1)\}/\bigl(f_3^2(1-f_3)^2\bigr)] \end{aligned} \tag{42}$$

where

$$\begin{aligned} P &= -(4/3)f + 3f^2 + (4/5)f^3 - (5/3)f^4 \\ P_1 &= x_1x_3K/(f_3f_4+1)(1-f_3) \\ P_2 &= Kf_3(4-3f_3) - K - 1 \\ P_3 &= x_1x_3K\{1-Kf_3(2-3f_3)\}/f_3(f_3f_4+1) \\ P_4 &= x_1x_3K\{1-2f_3(K+1)+2Kf_3^2(3-2f_3)\}/f_3(1-f_3)(f_3f_4(1-f_3)+1) \end{aligned} \tag{43}$$

All 'f' terms have been already defined by equation (35).

3.2. *Surface tension and surface segregation*

Surface tension of ternary system can be expressed in the form of three simultaneous equations by extending surface description of the binary systems [equation (20)]. This is given as

$$\sigma = \sigma_1 + (K_BT/\alpha)\ln(x_1^s/x_1) + (K_BT/\alpha)\ln(\gamma_1^s/\gamma_1) \tag{44a}$$
$$= \sigma_2 + (K_BT/\alpha)\ln(x_2^s/x_2) + (K_BT/\alpha)\ln(\gamma_2^s/\gamma_2) \tag{44b}$$
$$= \sigma_3 + (K_BT/\alpha)\ln(x_3^s/x_3) + (K_BT/\alpha)\ln(\gamma_3^s/\gamma_3) \tag{44c}$$

where σ_1, σ_2 and σ_3 are the surface tension of pure components comprising ternary system. γ_i^s $(i = 1, 2, 3)$ is the activity coefficient of ith component at the surface. Analytical expression of γ_i^s may be obtained by using equation (21) for the binary system. One may obtain surface tension and surface composition for the ternary system as a function of bulk concentration by using equations (40–42) in simultaneous equation (44) and solving it numerically.

4. Results and discussion

4.1. *Binary systems comprising Ag–Sn–Zn liquid alloys*

Large negative excess free energy of mixing (G_M^{xs}) values and phase diagrams [17] of Ag–Sn and Ag–Zn systems led us to treat them as compound forming (Ag_3Sn in Ag–Sn and AgZn in Ag–Zn) systems. On the other hand, Sn–Zn system is simple eutectic mixture and does not have large negative G_M^{xs}. In this case, it is assumed that diatomic clusters (Sn_2) exist in the melt.

4.1.1. Ag–Sn and Ag–Zn systems. Equations (8) and (15) have been used to calculate free energy of mixing, $G_M (= G_M^{xs} + G_M^{id}$; G_M^{id} being ideal free energy of mixing) of Ag–Sn (at $T = 1250$ K) and Ag–Zn (at $T = 1023$ K) liquid alloys, respectively. Required inputs for the calculation are interaction energy parameters. These have been set as

$$\text{For Ag}-\text{Sn} \quad w = 0.798\, K_B T,\ \Delta w_{AB} = -3 K_B T \quad \text{and} \quad \Delta w_{AA} = 0$$

$$\text{For Ag}-\text{Zn} \quad w + Z\Delta\varepsilon_{AB} = -2.065\, K_B T$$

G_M *versus* C_{Ag} along with respective experimental points [17] have been presented in figure 1. Theory agrees well with the experiment [17] in both cases. Larger values of G_M

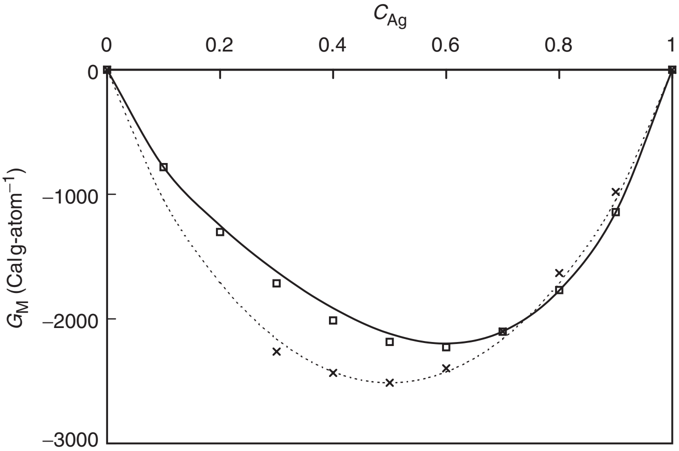

Figure 1. Free energy of mixing (G_M) for Ag–Sn and Ag–Zn liquid alloys. Ag–Sn system at $T = 1250$ K: (——) theory, (□□□□) reference [17]; Ag–Zn system at $T = 1023$ K: (·········) theory, (××××) reference [17].

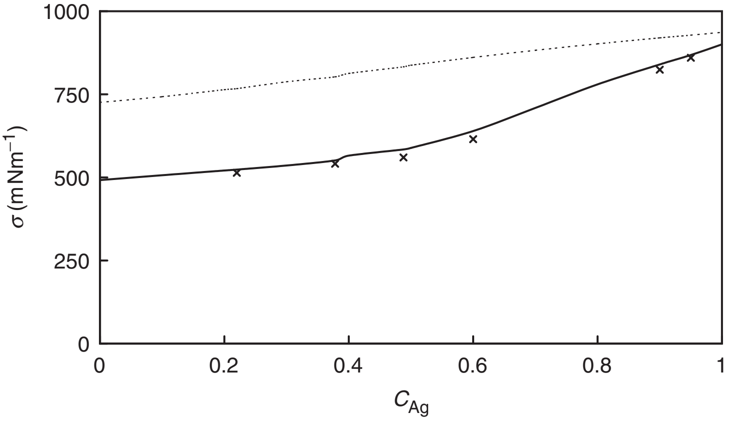

Figure 2. Surface tension (σ) for Ag–Sn and Ag–Zn liquid alloys. Ag–Sn system at $T = 1250$ K: (——) theory, (××××) reference [26]; Ag–Zn system at $T = 1023$ K: (······) theory.

with almost symmetrical behavior suggest the existence of 1 : 1 compound (AgZn) in the melt of Ag–Zn while asymmetrical nature of the graph with minima around $C_{Ag} = 0.6$ is indicative of the presence of 3 : 1 (Ag_3Sn) compounds in Ag–Sn system. In order to understand surface phenomenon in both systems, we have calculated surface tension (σ) and surface composition (C_i^s) via equations (22) and (23) by using same set of interaction energy parameters, as those used for the calculation of G_M. The surface tension values for the pure components have been taken from Smithell's metal reference book [24]. The mean atomic surface area, α has been calculated from the relation [25] ($\alpha = 1.12\,N^{-2}\,\Omega^{2/3}$; Ω is the molar volume of the alloy). In view of unavailability of experimental values, we have taken linear values for the volume of the system. The computed values of σ for both the systems have been given in figure 2 along with experimental points [26] wherever available. There is good agreement between theory and experiment [26] in case of Ag–Sn system. However, we could not compare our theoretical results for Ag–Zn system for want of experimental values. An increase in σ for both systems is observed with the increase of the concentration of Ag-component. The σ for Ag–Sn is lower than the ideal values at all concentrations while Ag–Zn system exhibits almost ideal behavior. Variation of surface concentration for both the systems has been depicted in figure 3. The surface of Ag–Sn system is quite enriched with Sn-atoms while Ag–Zn system exhibits the segregation of Zn atoms at the surface. This might be happening due to surface tension effect.

4.1.2. Sn–Zn system. G_M of Sn–Zn liquid alloys at $T = 900$ K has been calculated by using equation (17) whereas simultaneous equation (25) have been solved numerically to obtain surface tension (σ) and surface composition (C_i^s) as a function of bulk composition. Required input parameters for the calculation are ordering energy (w), mean atomic surface area (α) and surface tension values for the pure components (σ_i). w has been fixed as equal to 0.648 K_BT and α has been calculated following the procedure as described for Ag–Sn and Ag–Zn systems. The σ_i has been taken from Smithell's metal reference book [24]. Following the assumption that Sn_2 atoms exist in

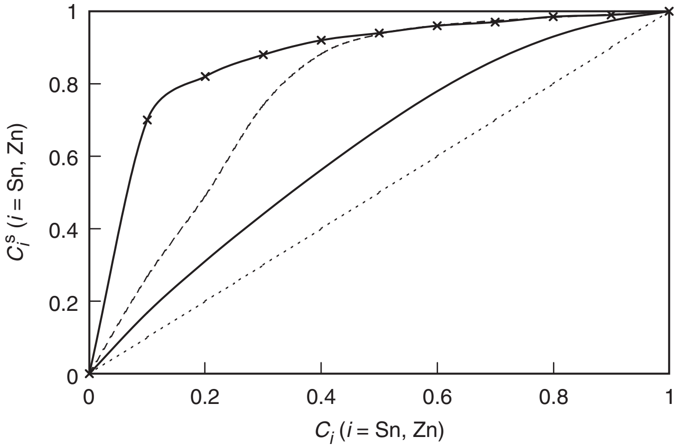

Figure 3. Surface composition (C_i^s) of concerned binaries of Ag–Sn–Zn liquid alloy. C_{Sn}^s *vs.* C_{Sn} for Ag–Sn system at $T = 1250$ K: (- - - -), C_{Sn}^s *vs.* C_{Sn} for Sn–Zn system at $T = 723$ K: (—×—), C_{Zn}^s *vs.* C_{Zn} for Ag–Zn system at $T = 1023$ K: (———) and (······) ideal values.

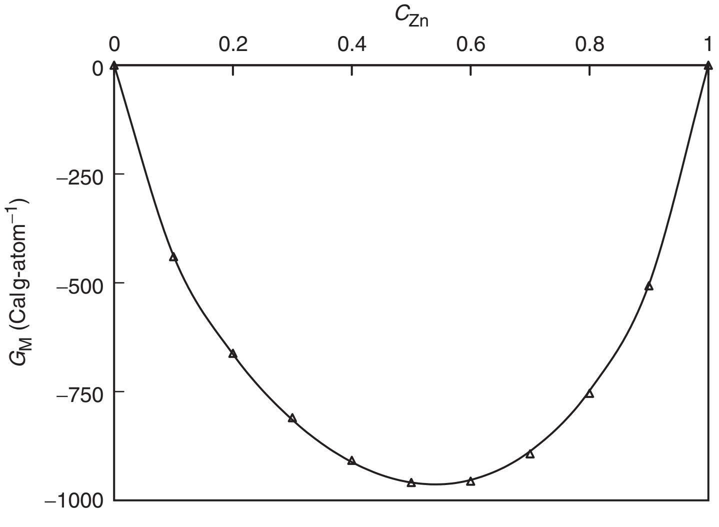

Figure 4. Free energy of mixing (G_M) for Sn–Zn liquid alloy at $T = 900$ K: (——) theory, (△△△△) reference [17].

the melt, we have taken $i = 2$ and $j = 1$. It is clear from figures 4 and 5 that computed values of G_M as well as σ agree well with the experimental points [17,27]. As regards experimental values of G_M, Hultgren *et al.* [17] have given the values at $T = 750$ K. In view of the temperature ($T = 900$ K) of Ag–Sn–Zn system to be investigated, we took the temperature of Sn–Zn system equal to that. Since the entropy [17] of Sn–Zn system was found to be temperature independent, recalculations were done for $T = 900$ K and obtained values were used for the comparison. Reproduction of experimental points by our model substantiates the assumption of the existence of diatomic tin in the melt.

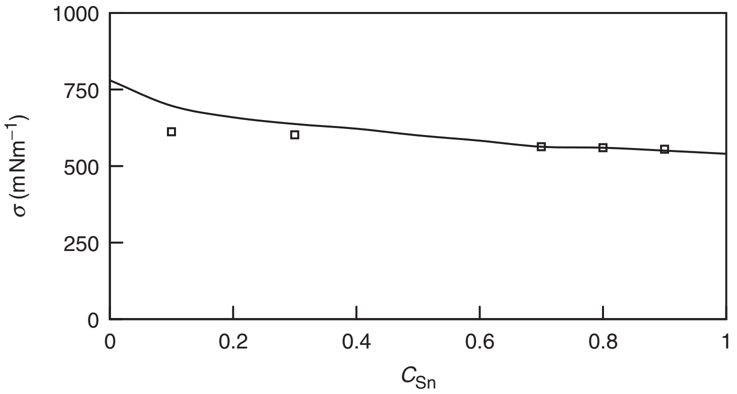

Figure 5. Surface tension (σ) for Sn–Zn liquid alloy at $T = 723$ K: —— theory, (□□□□) reference [27].

The σ of Sn–Zn alloy (figure 5) decreases with the increasing concentration of Sn-component, decrease being steeper up to 20% Sn. There is reasonable agreement between theory and experiment [27]. Our theoretical investigation suggests the segregation of Sn-atoms to the surface (figure 3). Of all binaries of Ag–Sn–Zn systems, Sn–Zn and Ag–Sn exhibits the segregation of Sn-atoms at the surface while in case of Ag–Zn, the segregation of Zn atoms is noticed. The degree of segregation of Sn-atoms in Sn–Zn liquid alloys is higher as compared to Ag–Sn system.

4.2. *Ag–Sn–Zn liquid alloys*

The free energy of mixing (ΔG_M) of ternary Ag–Sn–Zn liquid alloys at $T = 900$ K has been calculated via equation (34) for three cross section with constant Ag to Sn ratio, i.e. Ag : Sn = 1 : 1, 1 : 3, and 3 : 1. The calculation requires interaction energy parameters of concerned binaries (Ag–Sn, Sn–Zn and Ag–Zn). In view of difference in the temperature of investigation of the ternary system and some concerned binaries such as Ag–Sn and Ag–Zn, we have made slight change in the magnitude, which are comparable to the values taken for binary investigation. Assuming Ag ≡ 1, Sn ≡ 2 and Zn ≡ 3, these are given as

$$\begin{aligned} w_{12} &= 0.928 K_\mathrm{B} T \\ \Delta w_{12} &= -2.87 K_\mathrm{B} T \\ w_{23} &= 0.648 K_\mathrm{B} T \\ w_{31} &= -1.765 K_\mathrm{B} T \end{aligned}$$

The similarity coefficients (ξ_{ij}) and correlative terms $\eta_{i(ij,\,ik)}$ required for the computation have been calculated through equations (31) and (33). It will be proper to mention that expressions for $\eta_{i(ij,\,ik)}$ involves the expression of G_M^xs for the concerned binaries, i.e. i–j and i–k, which have been taken from section 2. These are

$$\eta_{1(12,13)} = 271241.9, \quad \eta_{2(23,21)} = 310428.8 \quad \text{and} \quad \eta_{3(31,32)} = 616331$$
$$\xi_{12} = 0.4663152, \quad \xi_{23} = 0.3349614 \quad \text{and} \quad \xi_{31} = 0.6944004$$

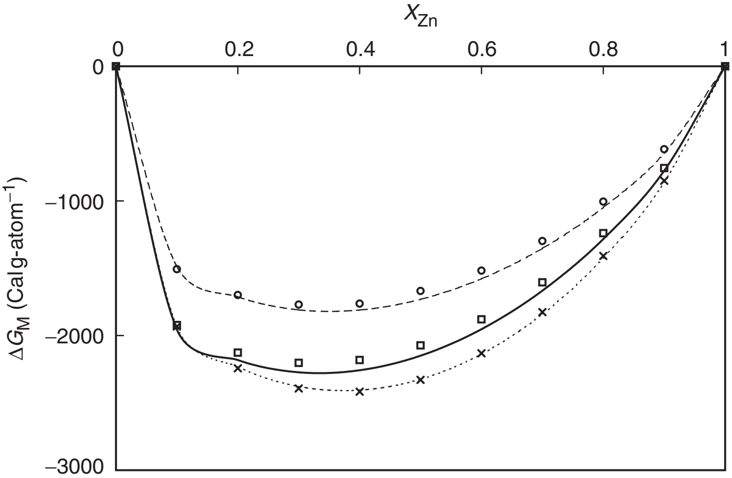

Figure 6. Free energy of mixing (ΔG_M) for Ag–Sn–Zn liquid alloy at $T = 900$ K for three cross section of constant Ag to Sn ratio: For Ag : Sn = 1 : 3 (- - - - -) theory, (○ ○ ○ ○) reference [28]; for Ag : Sn = 1 : 1 (——) theory, (□□□□) reference [28] and for Ag : Sn = 3 : 1 (·······) theory, (××××) reference [28].

The correctness of these values has been checked through the following relation

$$\xi_{12}\xi_{23}\xi_{31} = (1 - \xi_{12})(1 - \xi_{23})(1 - \xi_{31}) = 0.1084636$$

The computed values of ΔG_M have been presented in figure 6 along with experimental points [28]. It is clear from figure 6 that theoretical model reproduces the experimental observation. ΔG_M becomes less negative in the order of Ag : Sn = 3 : 1 → Ag : Sn = 1 : 1 → Ag : Sn = 1 : 3. In order to have complete picture of alloying in this system, we also investigated the concentration dependence of the surface tension (σ) and surface compositions (x_i^s) by using equations (40–44) in conjunction with equation (21). Linear values for the molar volume of the ternary system have been taken for the calculation of mean atomic surface area, α. Same set of interaction energies as those used for the calculation of bulk properties has been used for the calculation of surface properties. Numerical solutions of simultaneous equations (44a–c) not only give σ but also surface concentration (x_i^s). The computed values of σ for all the cross sections (Ag : Sn = 1 : 1, 1 : 3 and 3 : 1) have been presented in figure 7. For want of experimental values, our results could not be compared. The σ for the cross section Ag : Sn = 1 : 1 decreases slightly up to $x_{Zn} \approx 0.4$ and then increases with the increase of Zn-component. But no appreciable change in σ for Ag : Sn = 1 : 3 is observed up to 25% Zn. Less values of σ and sharp decrease in it up to $x_{Zn} \approx 0.5$ make Ag–Sn–Zn system with cross section 3 : 1 different from other cross sections, i.e. 1 : 1 and 1 : 3. The surface of Ag–Sn–Zn system for all cross section (figure 8) is quite enriched with Sn-atoms. Of all cross sections, Ag : Sn = 3 : 1 exhibits less segregation of tin to the surface. For comparison sake, x_{Zn}^s *versus* x_{Zn} has been plotted in figure 9. Decrease in the concentration of Zn at the surface has been observed for all bulk concentrations. Addition of Zn to binary Ag–Sn system causes further increase in the concentration of Sn-atoms to the surface and depletion of Zn-atoms.

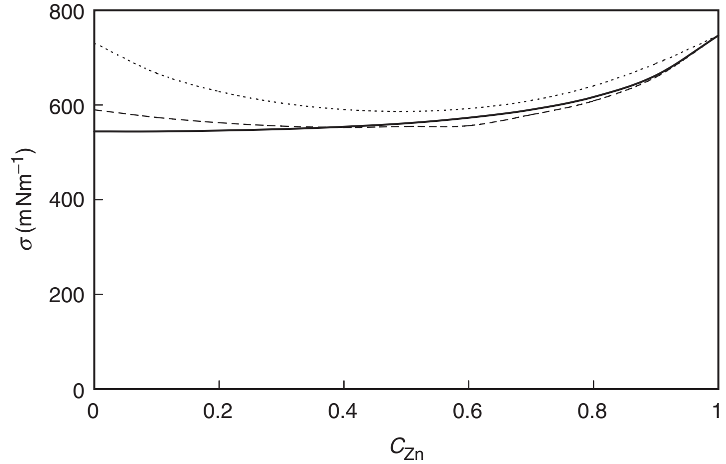

Figure 7. Surface tension (σ) for Ag–Sn–Zn liquid alloy at $T = 900\,\mathrm{K}$ for three cross section of constant Ag to Sn ratio: (——) for Ag : Sn = 1 : 3, (- - - - -) for Ag : Sn = 1 : 1 and (······) for Ag : Sn = 3 : 1.

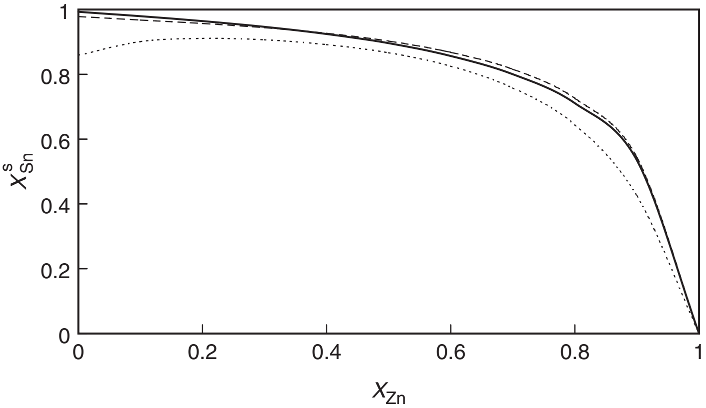

Figure 8. Surface concentration of Sn (x^{s}_{sn}) with bulk concentration (x_{Zn}) for three cross section of constant Ag to Sn ratio: (——) for Ag : Sn = 1 : 3, (- - - - -) for Ag : Sn = 1 : 1 and (······) for Ag : Sn = 3 : 1.

5. Conclusion

Our theoretical investigation of concerned binaries (Ag–Sn, Sn–Zn and Ag–Zn) of the ternary Ag–Sn–Zn liquid alloys not only reproduces experimental results, but suggests the presence of chemical short range order in Ag–Sn and Ag–Zn systems leading to the formation of compounds (Ag_3Sn in Ag–Sn and AgZn in Ag–Zn) in the melt. So far as Sn–Zn system is concerned, it shows the presence of diatomic tin in the melt. The surface tension, σ for Ag–Sn and Ag–Zn systems increases with the increase of the concentration of Ag-component. Ag–Zn system is different from Ag–Sn system in the sense that its σ shows almost ideal behavior. In case of Sn–Zn system, σ decreases with the addition of Sn-component. The surface of Ag–Sn and Sn–Zn are quite enriched with tin atoms whereas Ag–Zn system exhibits the segregation of Zn-atoms at the surface. Above findings of binary systems have been used to investigate the bulk as well as

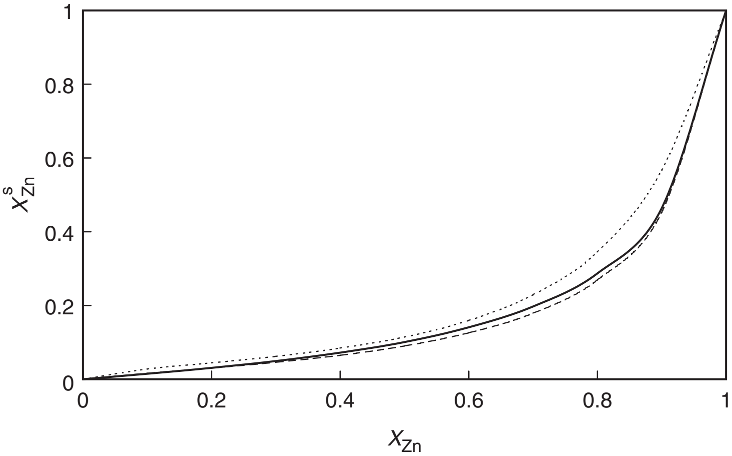

Figure 9. Surface concentration of Zn (x^s_{Zn}) with bulk concentration (x_{Zn}) for three cross section of constant Ag to Sn ratio: (——) for 1 : 3, (- - - - -) for 1 : 1 and (······) for 3 : 1.

surface properties of the ternary Ag–Sn–Zn liquid alloys through the application of a geometrical model in which binary compositions have been selected by considering the correlation of *i*th component with other components (*j* and *k*) of the ternary system. This mode of selection gives an improved model for the ternary system.

Application of this improved model to Ag–Sn–Zn system for three cross section, i.e. Ag : Sn = 1 : 1, 1 : 3, and 3 : 1 reproduces the experimental results for ΔG_M. It will be proper to mention that same set of interaction energies as those used for the bulk and surface calculations of binary systems have been used to investigate the bulk and surface phenomenon in ternary Ag–Sn–Zn liquid alloys. The variation of the computed surface tension (σ), though not compared with experimental values due to unavailability of data, is different for different cross sections. The σ for the cross section Ag : Sn = 1 : 1 decreases slightly up to $x_{Zn} \approx 0.4$ while for the cross-section Ag : Sn = 1 : 3, it remains almost constant up to 25% Zn. In case of the cross section Ag : Sn = 3 : 1, the decrease in σ is sharp up to 50% Zn. The magnitude of σ for Ag : Sn = 3 : 1 is higher at all concentrations compared to those Ag : Sn = 1 : 1 and 1 : 3. Our study also suggests that the surfaces of Ag–Sn–Zn system for all the cross section are quite enriched with Sn-atoms. Of all cross sections, Ag : Sn = 3 : 1 exhibits less segregation of tin to the surface. There is depletion in the concentration of Zn at the surface for all bulk concentrations.

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