Theoretical Investigation of Surface Tension and Viscosity of Zn-In Alloy at Different Temperatures Using Optimization Method

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Abstract The surface tension is calculated using Butler's equation and Layered structure approach. Viscosity is obtained from Singh and Sommer's formulation, Moelwyn-Hughes equation and Kaptay equation at different temperatures. we have computed interchange energy by estimating the best fit experimental and theoretical values at 700K using Flory's model. Taking these values of interchange energy at 700K, interchange energy at different temperatures are calculated using optimization method. Using values of interchange energy at different temperatures, heat of mixing, entropy of mixing and free energy of mixing at corresponding temperatures are computed. The partial excess free energy is calculated with the help of values of free energy of mixing which is used to find surface tension.

Keywords Flory's model, Surface tension, Viscosity, Order energy parameter, Different temperatures, Optimization method

1. Introduction

Zn-In alloy does not form intermetallic compounds and hence does not show brittle nature. It may be useful as a reliable high temperature lead free solder and alkaline battery anode [1]. It can be used in a protective molding to avoid reaction with moisture. The alloy exhibits good mechanical, electrical and thermal conductivity properties than its constituent components.

In metallurgical science, the study of surface and transport properties of liquid alloy is important because a good knowledge of their mixing properties in the liquid state is necessary for preparation of desired materials. Surface tension is required to understand the surface related phenomena such as wetting characteristics of solders, corrosion and kinetics of transformation. We have used Butler's equation [2] and Layered Structure approach [3], [4] to study the surface tension. And, viscosity is important for many metallurgical process and heterogeneous chemical reactions. The viscosity is studied with the help of Moelwyn-Hughes equation [5], Kaptay equation [4] and, Singh and Sommer's Formulation [6].

In this work, we have used Flory's model [7], [8] to explain the thermodynamic and structural behavior of the alloy at different temperatures because the size effect is noticeable in the alloys. In Flory's model, the interaction energy parameter is considered as temperature dependent and is determined by fitting experimental free energy of mixing at different concentrations. The mixing behavior of binary liquid alloys may be explained in terms of thermodynamic and microscopic properties. Thermodynamic behavior of the alloy is understood by the knowledge of free energy of mixing (G_M), activity (a), heat of mixing (H_M) and the entropy of mixing (S_M). Theory of Flory's model has been presented in section 2, result and discussion is dealt in section 3, and conclusions are provided in section 4.

2. Formalism

The alloying behavior of liquid alloys can be studied with the help of either the electronic theory of mixing [9-10] or the statistical mechanical theory of mixing. Metal physicists [11-13] have keen interest in explain the concentration dependent asymmetry in the properties of mixing of binary liquid alloys and hence to extract additional microscopic information. Whenever there is difference in size of the atomic species in a liquid alloy, Flory's model is best applicable for the determination of thermodynamic and microscopic properties since it has taken size mismatch into consideration.

Flory's expression for the free energy of mixing of a binary mixture A-B consists of C_A ($\equiv c$) mole of A and C_B {$\equiv$ c(1-c)} mole of B respectively, where C_A and C_B are the mole fractions of A ($\equiv$ Zn) and B ($\equiv$ In) in the binary liquid alloy A-B. Thus free energy of mixing of those alloys whose constituent atoms differ widely in size can be expressed as

$$G_M = G(ideal) + G(size) + c(1-c)G(\omega) \quad (1)$$

Where, $G(id) = RT[clnc + (1-c)ln(1-c)]$ (2)

G(size) and G(ω) are contributions due to the size effect and the interchange energy respectively which can be written from Flory's model as

$$\beta = 1 - 1/\Phi \text{ and } \Phi = \vartheta_B / \vartheta_A \quad (3)$$

$$G(\omega) = 1/(1 - \beta c) \quad (4)$$

$$G(size) = RT[cln(1-\beta) - ln(1-\beta c)] \quad (5)$$

Where, ϑ_A and ϑ_B are atomic volumes of the pure species A and B respectively [7] defined as

$$\vartheta_{Zn} = \vartheta_M [1+\alpha_p(T-T_M)] \text{ and } \vartheta_{x(X= Cd,In)} = \vartheta_M [1+\alpha_p(T-T_M)](6)$$

Where,

ϑ_M = atomic volume at melting point

T_M = melting temperature and

α_p = volume coefficient at constant temperature.

From Flory's model the expression for free energy of mixing is given by

$$G_M = RT\left[c \ln c + (1-c)ln(1-c) + c \ln(1-\beta) - ln(1-\beta c)\right] + \frac{\omega c(1-c)}{(1-\beta c)} \quad (7)$$

The activity a_A of the element A in the binary liquid alloy is given as,

$$lna_A = ln [c (1-\beta) \eta(c)] + \beta(1-c) \eta(c) + (1-c)^2 \eta^2(c)\omega/RT \quad (8)$$

The temperature derivative of G_M gives an expression for integral entropy of mixing

$$S_M = -RG(id) - RG(size) - c(1-c)\eta(c).\frac{\partial \omega}{\partial T} + RTc(1-c)\eta(c) \times [\beta/(1-\beta) - c\eta(c). \omega/RT].\partial\beta/\partial T \quad (9)$$

Where,

$$\partial\beta/\partial T = (\alpha^B - \alpha^A).v_A/v_B \quad (10)$$

and

$$\eta(c) = 1/(1 - \beta c) \quad (11)$$

where, α^A and α^B are the coefficients of thermal expansion of pure species A and B respectively.

First term in the right hand side in the equation (9) is due to ideal term and the second term is due to size factor (ϕ). The third and fourth term represents the temperature derivative terms of size factor and interchange energy. The necessity of taking ω as temperature dependent was noticed [9] and [14].

Now, heat of mixing can be obtained from equation (1) and (9) from standard thermodynamic relation,

$$\frac{H_M}{RT} = \frac{S_M}{R} + \frac{G_M}{RT} \quad (12)$$

$$\frac{H_M}{RT} = cln \, c + (1-c)ln(1-c) + c \ln(1-\beta) - ln(1-\beta c) + \frac{c(1-c)}{(1-\beta c)}.\frac{\omega}{RT} - \alpha(c) - \Phi(c) - \frac{1}{R}\frac{c(1-c)}{(1-\beta c)}.\frac{\partial \omega}{\partial T} + \frac{Tc(1-c)}{(1-\beta c)}.[\frac{\beta}{(1-\beta)} - \frac{c}{(1-\beta c)}\frac{\omega}{RT}].\frac{\partial \beta}{\partial T} \quad (13)$$

where,

$\alpha(c) = [clnc + (1-c)ln(1-c)]$ &

$\phi(c) = [cln(1-\beta) - ln(1-\beta c)]$

2.1. Viscosity

The Moelwyn – Hughes equation:-

Viscosity of liquid alloys helps to understand the mixing behavior of binary liquid alloys at microscopic level. It is one of the important transport properties. In order to examine the atomic transport behavior of the alloy, we have used the Moelwyn-Hughes equation [5].

The Moelwyn-Hughes equation for viscosity of liquid mixture is given as

$$\eta = (c_1\eta_1 + c_2\eta_2)(1 - 2c_1c_2.\frac{H_M}{RT}) \quad (14)$$

Where, η_K is the viscosity of pure component K and for most liquid metals, it can be calculated from Arrhenius type equation [15] at temperature T as

$$\eta_K = \eta_{OK} \, exp\left[\frac{E_n}{RT}\right] \quad (15)$$

Where, η_{OK} is constant (in unit of viscosity) and E_n is the energy of activation of viscous flow for pure metal (in unit of energy per mole).

Singh and Sommer's Formulation:-

According to Singh and Sommer [6], the deviation in the viscosity of a binary liquid alloy from the ideal mixing can be discussed quantitatively in terms of the energetic and the size factor. It is expressed as

$$\eta = \eta^0\phi \quad (16)$$

Where, η^0 is prefactor and ϕ is a function of composition.

Moelwyn – Hughes [5] assumed a linear behavior of the prefactor, η^0 and approximated as

$$\eta^0 = \sum_K c_K\eta_K \quad (17)$$

Where, c_K and η_K are the concentration of component and viscosity of pure component k respectively. Osman and Singh [16] suggested that when entropic effects are considered, the factor ϕ, as function of composition, can be obtained calculation from the expression

$$\phi = 1 + c_A c_B(\gamma - 1)^2 (c_A + \gamma c_B)^{-2} \quad (18)$$

where, size factor $\gamma = \frac{\Omega_B}{\Omega_A}$, $\Omega_B > \Omega_A$, Ω_K is atomic volume.

Kaptay equation:-

The kaptay equation [17] for the viscosity of binary mixture has been derived taking account into the theoretical relationship between the activation energy of viscous glow and the cohesion energy of the alloy stating that in alloys with stronger cohesion energy the viscosity will increase, and not decrease. It is expressed as

$$\eta = \frac{hN_A}{\sum_K C_K \Omega_K + \Omega^E} \, exp \left[\frac{\sum_K C_K G_K^* - \theta . H_M}{RT} \right] \quad (19)$$

Where, h = Plank's constant, N_A is Avogadro's number, R is the ideal gas constant, Ω_K represents the molar volume, Ω^E is the excess molar volume upon alloy formation, G_K^* is the Gibb's energy of activation of the viscous flow in pure component K, H_M is enthalpy of mixing of the alloy, C_K (=A, B) represents concentration, and Θ is a constant whose value is taken to be 0.155±0.015 [4]. G_K^* of component K is expressed as

$$G_K^* = RT \, ln \left(\frac{\eta_k \Omega_K}{hN_A} \right) \quad (20)$$

Where, η_K is the viscosity of pure component K.

The variation of viscosity, η_K with temperature T from the Arrhenius type equation [16] is expressed as

$$\eta_K = \eta_{OK} \, exp \left[\frac{E_n}{RT} \right] \quad (21)$$

Where, η_{OK} is constant (in unit of viscosity) and E_n is the energy of activation of viscous flow for pure metal (in unit of energy per mole).

2.2. Surface Tension

Butler's equation:-

The surface tension of the initial melt has great influence on the formation of solid alloys by the solidification process. The surface properties help to understand metallurgical modeling, description and prediction of structure development during solidification in the binary alloys. In our work, the Butler's equation [2] is employed to study its surface tension. Butler's assumed the existence of surface monolayer at the surface of a liquid as a separate phase that is in thermal equilibrium with the bulk phase and derived an expression

$$\Gamma = \Gamma_1 + \frac{1}{A_1} \left(G_1^{E,s} - G_1^{E,b} \right) + \frac{RT}{A_1} \left[ln(1 - X_2^s) - ln(1 - X_2^b) \right]$$
$$= \Gamma_2 + \frac{1}{A_2} \left(G_2^{E,s} - G_2^{E,b} \right) + \frac{RT}{A_2} \left[ln(X_2^s) - ln(X_2^b) \right] \quad (22)$$

Where, Γ_1 and Γ_2 are the surface tension of the pure component 1 and 2 respectively. $G_i^{E,s}$ and $G_i^{E,b}$ (i = 1,2) are partial excess free energies, X_i^s and X_i^b are mole fraction of component i in the surface and bulk respectively The molar surface area of the component i can be computed by using the relation

$$A_i = K . N_A^{1/3} . V_i^{2/3} \quad (23)$$

Where, K (= 1.091) is geometrical factor for the liquid alloy [17]. For binary mixture, $X_1^b + X_2^b = X_1^s + X_2^s = 1$.

Layered Structure approach:-

The layered structure approach [3], [4] connects the surface tension (Γ) of alloy to its bulk thermodynamic properties through the bulk activity coefficients (Γ_k) as

$$\Gamma = \Gamma_k + \frac{K_B T}{A_K} \, ln \, \frac{C_K^S}{\gamma_K C_K} + \left[P(1 - C_K^S)^2 + q(1 - C_K)^2 \right] \frac{\omega}{A_K} \quad (24)$$

Where, K_B stands for Boltzmann constant; Γ_k is surface tension, C_K^S is the surface concentration of pure component K (K = A, B) at temperature T, p and q are surface coordination fractions, related as p + 2q = 1. In a simple cubic crystal $z = 6$, p = 2⁄3 and q = 1⁄6, in a bcc crystal $z = 8$, p = 3⁄5 and q = 1⁄5, and in a closely packed crystal, $z = 12$, p = 1⁄2 and q = 1⁄4 [3], [4]. And, A_K is the mean area of the surface per atom which can be computed as

$$A_{K=} \sum A_i C_i \ (i = A,B)$$

Where, $A_i = K . N_A^{1/3} . V_i^{2/3}$

2.3. Optimization of Free Energy of Mixing (G_M), Activity (a), Heat of Mixing (H_M), Surface Tension (Γ) and Viscosity (η)

The optimization method is a statistical thermodynamics or polynomial expressions. The adjustable coefficients, used in the process, are estimated by least square method.

The various thermodynamic properties, described by a power-series law whose coefficient are A,B,C,D,E,…..(say), are determined by least-square method [18]. The heat capacity can be expressed as

$$C_P = -C - 2DT - 2ET^{-2} \quad (25)$$

From the thermodynamic relation, the enthalpy is given by

$$H = H(T_0) + \int_0^T C_P dT = A - CT - DT^2 + 2ET^{-1} - \quad (26)$$

Also, the entropy is given by

$$S = S(T_0) + \int_0^T \frac{C_P}{T} dT = -B - C(1 + lnT) - 2DT + ET^{-2} - \cdots \ldots \ldots \ldots \quad (27)$$

By using equation (18) and (20) in the thermodynamic relation, G= H − TS, we get the temperature (T) dependent free energy as

$$G = A + BT + CTlnT + DT^2 + ET^{-1} \ldots \ldots \ldots \ldots \quad (28)$$

The composition dependence of excess free energy of mixing is given by Redlich-Kister polynomial equation as

$$G_M^{XS}(c,T) = c(1-c) \sum_{l=0}^{m} K_l(T)[c - (1-c)]^l \quad (29)$$

With

$$K_l(T) = A_1 + B_1 T + C_1 TlnT + D_1 T^2 + \ldots \ldots \ldots (30)$$

The coefficients K_1 depends upon the temperature same as that of G in equation (22). The least-square method can be used to obtain the parameters involved in equation (23). For this purpose, the required excess free energy of mixing (G_M^{XS}) of the alloy liquid alloy at different temperatures can be determined by the relation

$$G_M^{XS} = G_M - G_M^{id} = RT[clnc + (1-c)ln\,(1-c) \quad (31)$$

The values for the free energy of mixing (G_M) of liquid alloys at different temperatures can be calculated from equation (1) by knowing the values of ordering energy parameter (ω) at different temperatures from the relation [19], [20]

$$\omega(T) = A + BT \quad (32)$$

Where, A and B are coefficient constants.

3. Result and Discussion

The values of A and B in equation are calculated with the help of values of ω/RT and $\frac{1}{R}\frac{\partial \omega}{\partial T}$ at 700K for Zn-In alloy using equation (32). These values of ω/RT and $\frac{1}{R}\frac{\partial \omega}{\partial T}$ at temperature 700K is computed using the best fit approximation of experimental values of the alloys from Hultgrenet.al. 1973 [21] using equations (7) and (9). The best fit parameters of the alloy at 700K is found to be $\omega/RT = 1.428$ using equation (7) and $\frac{1}{R}\frac{\partial \omega}{\partial T} = -0.39$ using equation (9). By taking the values of coefficient constants A, B, ω/RT and $\frac{1}{R}\frac{\partial \omega}{\partial T}$ the values of interchange energy (ω) at different temperatures (i.e. 700K, 800K, 950K, 1050K) are obtained.
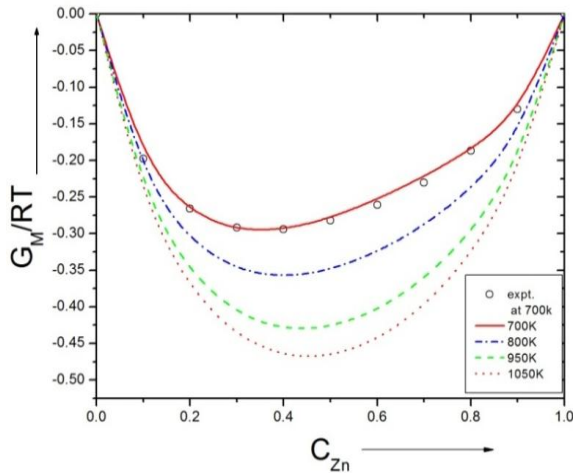
Table 1. Estimated values of order energy parameter at different temperatures in Zn-In liquid alloy

Temperature (T) in K	Order energy Parameter ω/RT
700	1.428
800	1.2007
950	0.9495
1050	0.8220

The values of free energy of mixing (G_M) of the alloy at temperatures 700K, 800K, 950K and 1050K have been calculated by using the corresponding values of $\omega(T)$ in equation (7) over the entire range of concentration. And, the values of free energy of mixing (G_M) are used to calculate the corresponding excess free energy of mixing (G_M^{XS}) of the alloy at temperatures of study by using equation (31).

Interaction energy (ω) is found to be positive for the Zn-In alloy, which indicates that is segregating in nature. Using above interchange energy (ω), we have computed free energy of mixing (G_M), activity (a) entropy of mixing (S_M), heat of mixing (H_M), surface tension (Γ) and viscosity (η) at temperatures 700K, 800K, 950K, 1050K using Flory's model in which size factor plays important role.

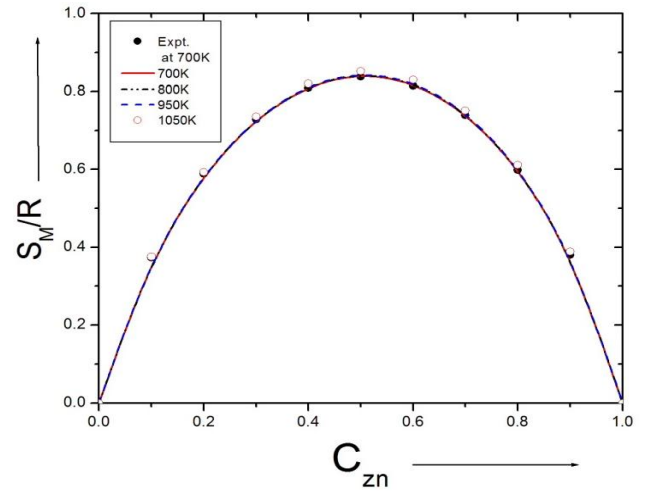### 3.1. Free Energy of Mixing (G_M)

Figure (1). Graph for G_M/RT versus the concentration of C_{Zn} of Zn-In liquid alloy at temperatures 700K, 800K, 950K and 1050K

The experimental values of free energy of mixing (G_M) is taken from Hultgren et.al. [21] by which we have estimated the interchange energy (ω) at that temperatures by best fit method using equation (7) i.e. $\omega = 1.428RT$ at 700K. The free energy of mixing (G_M) at different temperatures are obtained using equation (7) with the help of optimized values of energy order parameters $\omega(T)$ presented on the table 1. The plot of experimental values of free energy of mixing (G_M) at 700K and theoretical values at temperatures 700K, 800K, 950K, 1050K of the Zn-In liquid alloy with respect to the concentration of Zn is shown in figure (1).

3.2. Entropy of Mixing (S_M)

The experimental values of entropy of mixing(S_M) at at 700K for the alloy is taken for Hultgren et. al. [21]. The values of $\frac{1}{R}\frac{\partial \omega}{\partial T}$ estimated at the temperature using best fit method with the help of equation (9) i.e. $\frac{1}{R}\frac{\partial \omega}{\partial T} = -0.39$ at 700K. The entropy of mixing of the alloy at temperatures 700K, 800K, 950K, 1050K are calculated using equation (9) conjugation with equations (10) and (11) with the help of optimized values of energy order parameters $\omega(T)$ presented on the table 1. We obtained constant values of $\frac{1}{R}\frac{\partial \omega}{\partial T}$ from equation (25).

The plot of experimental values of entropy of mixing (S_M) at temperatures 700K, 800K, 950K and 1050K of the alloy with respect to the concentration of Zn is shown in figure (2).
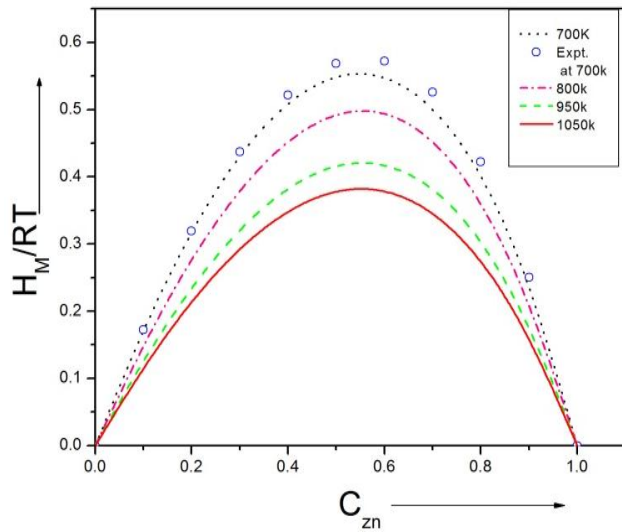

Figure (2). Graph for S_M/R versus the concentration of C_{Zn} of Zn-In liquid alloy at temperatures 700K, 800K, 950K and 1050K

3.3. Heat of Mixing (H_M)

The heat of mixing (H_M) for the alloys at temperatures 700K, 800K, 950K, 1050K are computed using equation (12) in conjugation with equations (7) and (9) with the help of corresponding optimized values of free energy of mixing (G_M) and entropy of mixing (S_M).

The plot of experimental values of heat of mixing (H_M) at 700K and theoretical values at temperatures 700K, 800K, 950K, 1050K of the Zn-In liquid alloy with respect to the concentration of Zn is shown in figure (3).

Figure (3). Graph for H_M/RT versus the concentration of C_{Zn} of Zn-In liquid alloy at temperatures 700K, 800K, 950K and 1050K

3.4. Excess FREE ENergy (G_M^{XS}), ACtivity (a) and PARTIAL EXCESS FREE ENergy ($\overline{G_M}^{XS}$)

The least-square method has been used to calculate the parameters involved in equation (29) at different temperatures and then the optimized coefficients for the alloys are computed which are listed in the table 2.

Table 2. Calculated values of optimized coefficients A_l, B_l, C_l and D_l (l=0 to 3) in liquid alloy Zn-In

Values of l	A_l (Jmole^{-1} k^{-1})	B_l (Jmole^{-1} k^{-1})	C_l (Jmole^{-1} k^{-1})	D_l (Jmole^{-1} k^{-1})
0	10.618292	-0.094818	0.013053	-4.9992E-06
1	2.808904	-0.025174	0.003467	-1.32891E-06
2	0.762508	-0.006876	0.000947	-3.63581E-07
3	0.201029	-0.001825	0.000251	-9.66686E-08

We have used the parameters i.e. K_o, K_1, K_2 and K_3 to obtain partial excess free energy using equation (29). The partial excess free energy of mixing ($\overline{G_M}^{XS}$) of the components A(=Zn) and B(=In) are computed using equations [19]

$$\overline{G}_{M,A}^{-XS}(C,T)=(1-C)^2 \sum_{l=0}^{m} K_l(T)[\,(1+2l)c - (1-c)](2c-1)^{l-1} \tag{33}$$

and

$$\overline{G}_{M,B}^{-XS}(C,T)=C^2 \sum_{l=0}^{m} K_l(T)[\,c - (1+2l)(1-c))](2c-1)^{l-1} \tag{34}$$

The partial excess free energy of mixing of the components i.e. Zn and In involved in Zn-In liquid alloys at temperatures 700K, 800K, 950K, 1050K have been calculated separately over the entire concentration range by equations (33) and (34) with the help of optimized coefficients i.e. K_o, K_1, K_2 and K_3. The values of partial

excess free energy of mixing of the components in Zn-In alloy at temperatures 700K, 800K, 950K, 1050K are shown in table 3, table 4, table 5 and table 6.

Table 3. The values of partial excess free energy of mixing of the components at 700K of Zn-In alloy

Zn-In alloy at 700K		
C_{Zn}	$\dfrac{\overline{G}_{M,Zn}^{XS}}{RT}$ (J/mole)	$\dfrac{\overline{G}_{M,In}^{XS}}{RT}$ (J/mole)
0.1	1.158125	0.008149
0.2	1.000494	0.036235
0.3	0.84013	0.090022
0.4	0.680171	0.176606
0.5	0.523363	0.305563
0.6	0.37321	0.490096
0.7	0.235119	0.748186
0.8	0.117553	1.103738
0.9	0.033174	1.587732

Table 4. The values of partial excess free energy of mixing of the components at 800K of Zn-In alloys

Zn-In alloy at 800K		
C_{Zn}	$\dfrac{\overline{G}_{M,Zn}^{XS}}{RT}$(J/mole)	$\dfrac{\overline{G}_{M,In}^{XS}}{RT}$(J/mole)
0.1	0.958598	0.006742
0.2	0.828181	0.029979
0.3	0.695471	0.074491
0.4	0.563065	0.146161
0.5	0.433245	0.252925
0.6	0.308925	0.405709
0.7	0.194599	0.619383
0.8	0.097279	0.913700
0.9	0.027448	1.314244

Table 5. The values of partial excess free energy of mixing of the components at 950K of Zn-In alloys

Zn-In alloy at 950K		
C_{Zn}	$\dfrac{\overline{G}_{M,Zn}^{XS}}{RT}$(J/mole)	$\dfrac{\overline{G}_{M,In}^{XS}}{RT}$(J/mole)
0.1	0.732773	0.005185
0.2	0.645697	0.023064
0.3	0.541976	0.05733
0.4	0.435714	0.112532
0.5	0.333943	0.19480
0.6	0.239454	0.312564
0.7	0.153621	0.47728
0.8	0.079234	0.704152
0.9	0.023326	1.012857

Using these optimized partial excess free energy of mixing of both the components of the alloy, we have calculated the corresponding excess free energy of the alloy at different temperatures over the entire range of concentration from the relation.
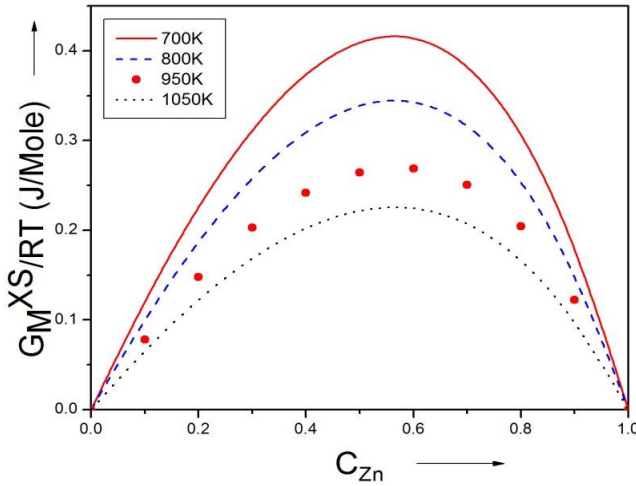
$$G_M^{XS} = C \overset{-XS}{G_{M,A}} + (1 - C) \overset{-XS}{G_{M,B}} \tag{35}$$

Table 6. The values of partial excess free energy of mixing of the components at 1050K of Zn-In alloys

Zn-In alloy at 1050K		
C_{Zn}	$\dfrac{\overset{-XS}{G_{M,Zn}}}{RT}$ (J/mole)	$\dfrac{\overset{-XS}{G_{M,In}}}{RT}$ (J/mole)
0.1	0.626864	0.004393
0.2	0.541802	0.01955
0.3	0.455151	0.048615
0.4	0.368607	0.095463
0.5	0.283679	0.165309
0.6	0.202298	0.265325
0.7	0.127432	0.405249
0.8	0.063697	0.597998
0.9	0.017969	0.860282

The optimized values of excess free energy of mixing for the alloys at temperatures 700K, 800K, 950K and 1050K over the entire concentration range is shown in figure (4).

Figure (4). Graph for $\frac{G_M^{XS}}{RT}$ at different temperatures versus C_{Zn} of Zn-In liquid at temperatures 700K, 800K, 950K and 1050K
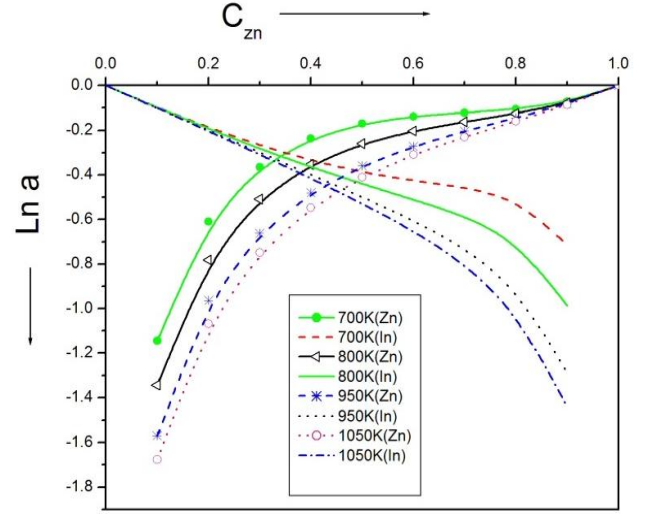
Now, the activity coefficients (γ_i), (i = Zn or In for Zn-In) at different temperature over the entire range of concentration for components have been computed from the relation

$$\overset{-XS}{G_{M,i}} = RT \ln \gamma_i \tag{36}$$

With
$$\gamma_i = \frac{a_i}{c_i} \tag{37}$$

Where, a_i and c_i be the activity and concentration of the components respectively of the Zn-In liquid alloy at corresponding temperature. Using equations (36) and (37) we have computed activities of the components of alloys at temperatures 700K, 800K, 950K and 1050K with the help of optimized values of partial excess free energy of the components that are presented on the table 3, table 4, table 5, table 6. The plot of activity is presented on graph (5).

Figure (5). Graph for Lna at different temperatures versus C_{Zn} of Zn-In liquid alloy 700K, 800K, 950K and 1050K

3.5. Surface Tension

The surface tension of the liquid alloys can be computed using equation (22) conjugation with equation (23) using Butler's model [2], [20]. The ratio of partial excess Gibbs energy in the bulk and that in the surface can be expressed as

$$\beta = \frac{G_i^{E,S}}{G_i^{E,b}}$$

The value of parameter β has been taken as 0.83 as suggested by different researchers to compute surface tension of liquid alloys i.e. Guggenheim [11], Yeum et al. [22] and Tanaka et al. [17]. The temperature coefficients and surface tension at melting points of pure Zn and In components are taken from Smithells Metal reference book [14]. The surface tension of the pure component at temperature of investigation have been calculated using the relation.
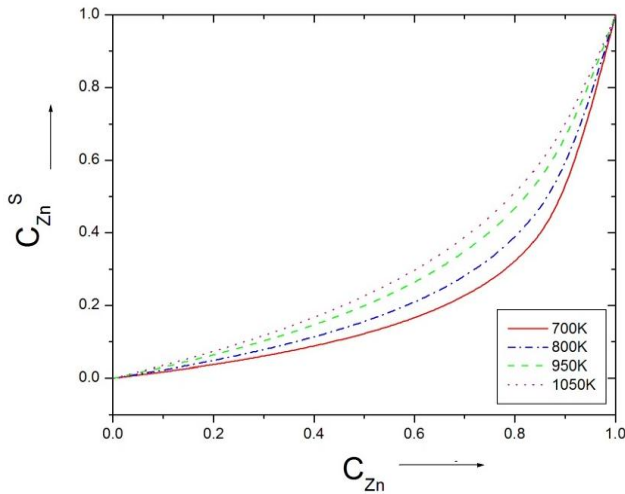
$$\Gamma(T) = \Gamma_m + \frac{\partial \Gamma}{\partial T}(T - T_m)$$

Where, $\frac{\partial \Gamma}{\partial T}$ (= -0.09 mNm^{-1}k^{-1} for In, and -0.17mNm^{-1}k^{-1} for Zn) is temperature coefficient of surface tension, Tm (= 430 K for In, and 692.5K for Zn) is melting temperature and T=700K, 800K, 950K and 1050K.
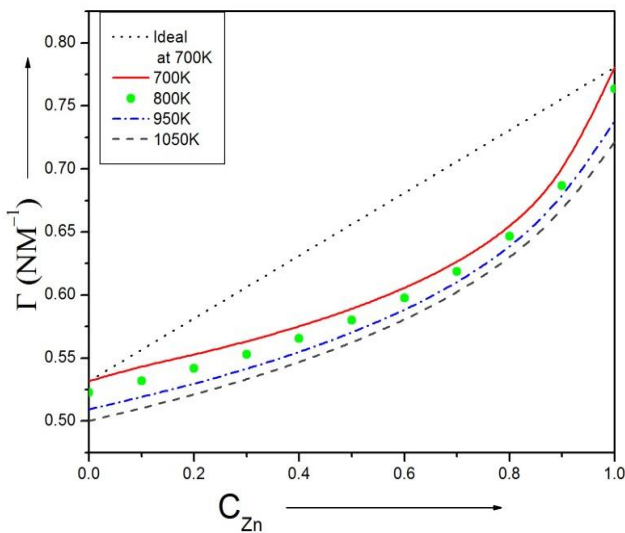
We have calculated surface concentration of Zinc corresponding to the bulk concentration of Zinc component in the alloys using Butler's equation (22). The plot of the surface concentration of Zinc Vs bulk concentration of Zn-In alloy at temperatures 700K, 800K, 950K and 1050K is shown in figure (6).

It is found from the analysis that the computed surface tension for Zn-In system at 700K is less than ideal value (= $X_1\Gamma_1 + X_2\Gamma_2$) at the concentrations from C_{Zn}=0.1 to 0.9 i.e. there is negative departure of surface tension from ideality at 700K. In Zn-In alloy, the surface tension of Pure Zinc component and pure Indium component at melting point [14] is taken to calculate the surface tension at different

temperatures. The surface tension of pure Zinc component is less than the surface tension of pure Indium component at temperature T (T=700K, 800K, 950K, 1050K). We have calculated the surface tension with the concentration of Zinc component in the alloy using Butler's equation (16) which indicates that as the concentration of Zinc component increases, surface tension increases at temperature T(T=700K, 800K, 950K, 1050K) which is shown in figure (7).
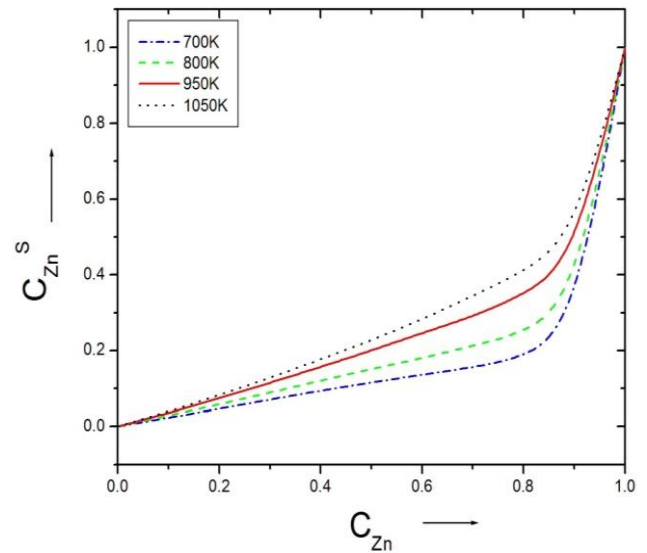

Figure (6). The surface concentration of Zn versus bulk concentration of Zn in Zn-In alloy at temperature 700K, 800K, 950K and 1050K using Butler's equation
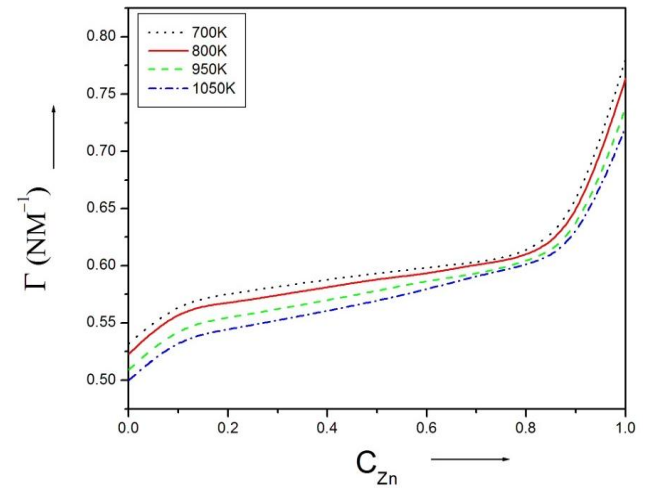

Figure (7). The surface tension (Γ) versus concentration of Zn at temperatures 700K, 800K, 950K, 1050K using Butler's equation

The surface tension of the alloy is calculated using Layered structure approach [3], [4] using equation (24) at temperatures 700K, 800K, 950K and 1050K. The plot of surface concentration of Zinc (C_{Zn}^S) versus the bulk concentration of Zinc (C_{Zn}) of the alloy is shown in figure (8) using Layered structure approach at different temperatures.

Figure (8). Surface concentration of Zinc (C_{Zn}^S) versus the bulk concentration of Zinc (C_{Zn}) of alloy Zn-In alloy at temperatures 700K, 800K, 950K and 1050K using Layered Structure approach

We have computed the surface tension of the alloys using these values of surface concentrations. The plot of the surface tension (Γ) versus the Concentration of Zinc of the alloy Zn-In is shown in figure (9) using Layered Structure approach at temperatures 700K, 800K, 950K and 1050K which shows temperature dependence.
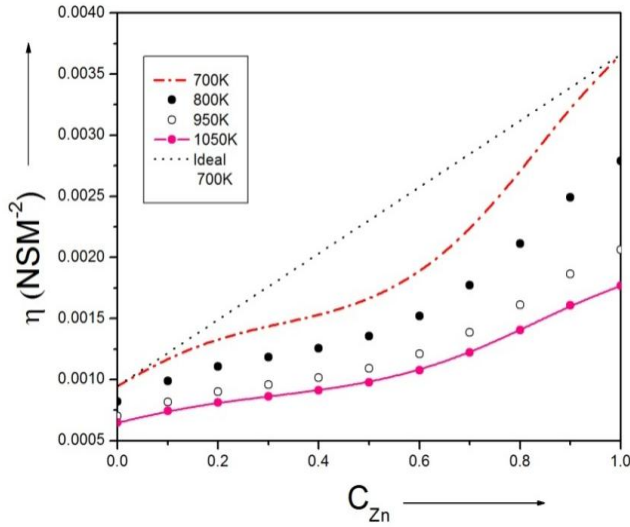

Figure (9). The surface tension (Γ) versus concentration of Zn of Zn-In alloy at temperatures 700K, 800K, 950K, 1050K using Layered Structure approach

In both model for the calculation of surface tension, it has been found that surface tension is temperature dependent and decrease with increase in temperature and vice-versa at each concentration range of zinc component.

3.6. Viscosity

The viscosity of alloys at temperatures 700K, 800K, 950K and 1050k are computed using Moelwyn-Hughes equation [3], [23] with the help of heat of mixing (H_M) at temperatures

700K, 800K, 950K and 1050K.Viscosity of pure components i.e. Zn and In at temperature T (T =700K, 800K, 950K, 1050K) of the alloy are calculated using equation (15) with the help of the value of the constants E and η_{ok} for the metals [15]. And, heat of mixing (H_M) at temperature T (T =700K, 800K, 950K, 1050K) are obtained using equation (12) in conjugation with equations (7) and (9) with the help of optimized values of interchange energy parameters(ω) presented on table 2. The viscosity of pure component of Zinc is greater than the viscosity of pure component of Indium in the alloy at temperature T. As the concentration of Zinc component in the alloy increases, the viscosity of the alloy increases at temperature T. The plot of the viscosity at different temperatures (i.e. 700K, 800K, 950K and 1050K) with the concentration of Zinc is shown in the figure (10).
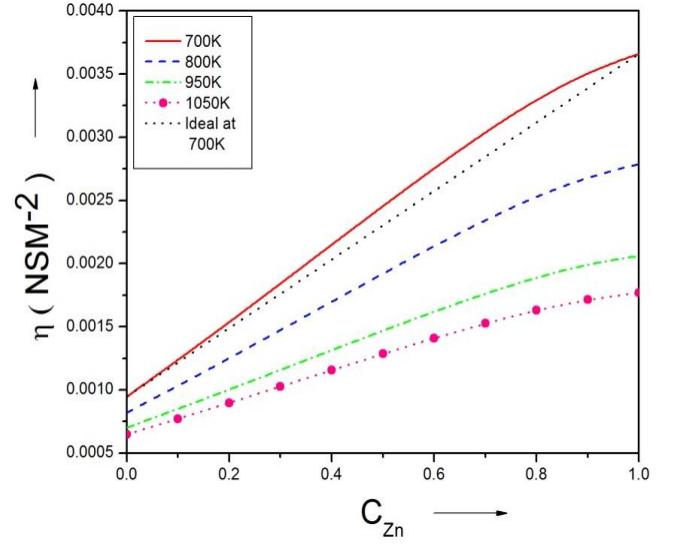

Figure (10). The viscosity of Zn-In liquid alloy versus concentration of Zinc at temperatures 700K, 800K, 950K, 1050K using Moelwyn-Hughes equation
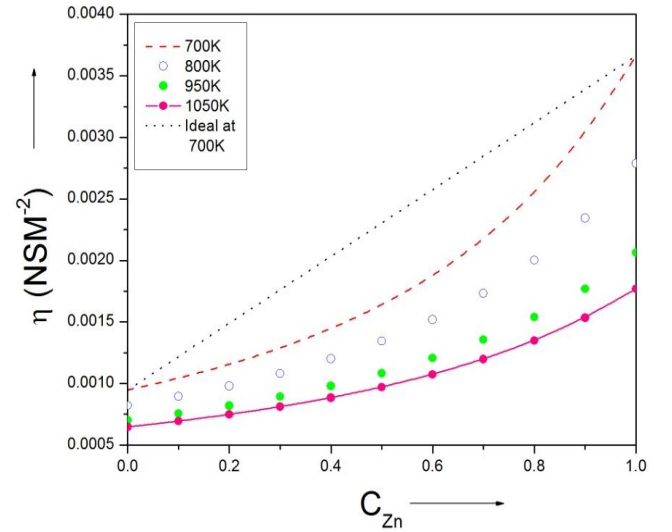
The viscosity of alloys at temperatures 700K, 800K, 950K and 1050k are computed using Singh and Sommer's formulation [6] with the help of equation (17) in conjugation with equation (18) taking the optimized values of heat of mixing (H_M) at different temperatures. Zn and In components in Zn-In alloy at temperature T (T =700K, 800K, 950K, 1050K) of the alloy are calculated using equation (15) with the help of the value of the constants E and η_{ok} for the metals [15]. For simplicity, we have ignored the value of the excess molar volume (Ω^E). The size factor plays important role to calculate viscosity which is computed using equation (6). The plot of the viscosity versus the concentration of Zinc component using Singh and Sommer's formulation is shown in figure (11).

We have used equation (19) in conjugation with equations (20) and (21) to find the viscosity using Kaptay equation [4] with the help of optimized values of heat of mixing (H_M) at different temperatures. In both alloys, Viscosity of pure components i.e. Zn and In components at temperature T (T =700K, 800K, 950K, 1050K) of the alloy are calculated using equation (21) with the help of the value of the

constants E and η_{ok} for the metals [15]. The plot of the viscosity versus the concentration of Zinc component using Kaptay equation is shown in figure (12).

Figure (11). The viscosity of Zn-In liquid alloy versus concentration of Zinc at temperatures 700K, 800K, 950K, 1050K using Singh and Sommer's Formulation

Figure (12). The viscosity of Zn-In liquid alloy versus concentration of Zinc at temperatures 700K, 800K, 950K, 1050K using Kaptay equation

From all different model for calculation of viscosity, We observed that it is temperature dependent. As the temperature of study increases, the viscosity of the alloy decreases and vice-versa at each concentration range of zinc component.

4. Conclusions

The interchange energy and size factor are temperature dependent which play important role in the mixing properties of the alloy using Flory's model. The alloy is symmetric and segregating in nature. Thermodynamic property of the alloy

is temperature dependent. The surface tension and viscosity of the alloy are temperature dependent and decrease as the temperature of study increase at each concentration range. The optimization method is useful to obtain a consistent set of theoretical model parameters which gives idea to predict into temperature and concentration region in which the direct experimental determination is unavailable.

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