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Theoretical Investigation for the Properties of Mixing of Zn-Cd Melts by Four-Parameter Model

Rajendra Prasad Chaudhary[1], Prakash Ranjan Deen[2], Soni Kumari[3], Ajay Kumar Pandey[3], Jagdhar Mandal[4*], Indu Shekhar Jha[1]

[1]Department of Physics, Mahendra Morang Adarsh Multiple Campus, Biratnagar, TU, Nepal
[2]Department of Physics, Purnea College, Purnia, Purnea University, Purnia, India
[3]Department of Physics, Purnea University, Purnia, India
[4]University Department of Physics, Tilka Manjhi Bhagalpur University, Bhagalpur, India
Email: r.p.chaudhary028@gmail.com; talk2deen@gmail.com; sonikrisharma2411@gmail.com; akpphysics01@gmail.com; jmandal1284@gmail.com; isjha12345@gmail.com

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Abstract

The four-parameter model (FPM) has been employed to investigate the thermophysical properties of Zn-Cd melts at 800 K. The analytical expressions deduced in the framework of FPM are applied to compute the concentration dependence of the excess free energy of mixing, free energy of mixing, activity coefficient, activity, heat of mixing, excess entropy of mixing, entropy of mixing, and concentration fluctuations of Zn-Cd melts at 800 K, which agree well with the correlated experimental data. The theoretical data of the short-range order parameter and excess stability function of Zn-Cd melts at 800 K are also determined relative to the composition. Again, the Butler model is employed in conjunction with FPM to investigate the concentration dependence of the surface concentration and surface tension of Zn-Cd melts at 800 K. Further, the Moelwyn-Hughes model coupled together with FPM is utilized to predict the concentration dependence of the diffusivity ratio and viscosity of Zn-Cd melts at 800 K. The theoretical results advocate that Zn-Cd melt at 800 K is a feebly segregating alloy.

Keywords

Four-Parameter Model, Gibbs Free Energy of Mixing, Concentration Fluctuations, Surface Tension, Viscosity

1. Introduction

The Zn-Cd system is a simple eutectic alloy possessing low melting point [1]. The

thermophysical behaviors *i.e.* enhanced hardness, mechanical strength, fatigue strength, wear resistance, corrosion resistance, etc are responsible for the potential applications of Zn-Cd system in technology, soldering, design of semiconducting compounds, packaging, etc [2]-[4]. The concentration dependent thermodynamic properties like excess free energy of mixing, G_M^{XS}, free energy of mixing, G_M, heat of mixing, H_M and entropy of mixing, S_M of Zn-Cd melts at 800 K are symmetric around the concentration, C= 0.5 [1]. The positive values of G_M^{XS}, and H_M as well as positive departures of activity, $a_i\left(i = Zn, Cd\right)$ [1] refer to the segregating nature of Zn-Cd melts at 800 K [5]. The interesting thermophysical behavior of Zn-Cd melts has drawn the attentiveness of several researchers [2] [4] [6]-[8]. The self-association model (SAM) [5] has been employed to explain G_M, activity a_{Zn}, concentration fluctuations, $S_{CC}\left(0\right)$, short-range order parameter (SRO), α_1, diffusivity ratio, $\frac{D_M}{D_{id}}$, surface concentration C_i^s, and surface tension, σ of Zn-Cd melts at 900 K [4]. It should be pointed out that G_M of Zn-Cd melts exhibits asymmetric behavior with respect to the concentration. The SAM model is further employed to investigate G_M, a_{Zn}, $S_{CC}\left(0\right)$, C_i^s, σ, surface concentration fluctuations, $S_{cc}^s\left(0\right)$, $\frac{D_M}{D_{id}}$ and excess viscosity, $\frac{\Delta\eta}{\eta^0}$ (where, η^0 is the ideal viscosity of the system) of Zn-Cd melts at different temperatures *i.e.* 773 K, 800 K and 923 K [7]. The quasi-chemical approximation (QCA) is applied to explain G_M, H_M, S_M, a_{Zn}, a_{Cd}, $S_{CC}\left(0\right)$, α_1, $\frac{D_M}{D_{id}}$, C_i^s, σ and $S_{cc}^s\left(0\right)$ [6]. The thermophysical properties like G_M, a_{Zn}, $S_{CC}\left(0\right)$, α_1, and $\frac{D_M}{D_{id}}$ of Zn-Cd melts have been theoretically analyzed on using molecular interaction volume model (MIVM) at 743 K, 800 K and 900 K [8]. However, the study of the excess entropy of mixing, S_M^{XS}, and activity coefficient, $\gamma_i\left(i = Zn, Cd\right)$, excess stability function, E^{XS} and viscosity, η is not available in the literature. Therefore in present work, a four-parameter model (FPM) [9] [10] has been employed to analyze the thermodynamic functions *i.e.* G_M^{XS}, G_M, H_M, S_M^{XS}, S_M, a_{Zn}, a_{Cd}, microscopic functions namely $S_{CC}\left(0\right)$, α_1 and E^{XS}, surface properties C_i^s, σ and transport like $\frac{D_M}{D_{id}}$ and viscosity, η for Zn-Cd melts at 800 K. For the analysis of the surface properties, Butler model [11] and for transport properties, Moelwyn-Hughes model [12] are applied in conjunction with FPM.

The basic concept of FMP [9] is dependent on Maclaurin infinite series. The integral thermodynamic functions of a binary solution A-B (say) may be described in terms of concentration separately in the neighborhood of pure of pure components A and B on employing appropriate boundary conditions. In past, FPM has been employed to investigate the thermophysical properties of

several compound forming liquid alloys like Bi-Mg, Mg-Pb, In-Na, Al-Cu, Fe-Si, Cu-Sn etc [9] [13]-[15] and segregating liquid alloys namely Bi-Zn, Ga-Zn, In-Zn, Sn-Zn, Al-Sn, Bi-Hg etc [9] [16] [17]. Therefore in present ingestion, FPM is taken into the consideration to analyze the properties of mixing of Zn-Cd melts at 800 K.

2. Formalism

The thermodynamic and structural properties of a binary solution can be analyzed on applying FPM [9] which is basically dependent on Maclaurin infinite series with suitable boundary conditions.

2.1. Thermodynamic and Microscopic Properties of Molten Binary System at a Given Temperature

Consider a binary solution A-B consisting of N_A and N_B atoms per mole of elements A and B respectively such that $N_A = NC_A$ and $N_B = NC_B$, where, $C_i\left(i \equiv A, B\right)$ denotes the concentration of the i^{th} component of solution.

The analytical expression for $\frac{G_M^{XS}}{RT}$ is deduced in the framework of FPM [9], [10] as

$$\frac{G_M^{XS}}{RT} = C_1C_2\left(a_1 + a_2C_2 + C_1C_2a_3 + C_1C_2^2a_4\right) \tag{1}$$

where, T = temperature (in K), R = molar gas constant, $C_A = C$ and $C_B = 1 - C$, $a_j\left(j \equiv 1,2,3,4\right)$ are the interaction parameters which are temperature dependent but independent of composition and pressure. The Equation (1) is used to determine the values of G_M^{XS} relative to the composition for a binary melt at a specified temperature.

For the i^{th} component, the activity coefficient, $\gamma_i\left(i = A, B\right)$ of a binary solution is given by [5] [9]

$$RT\ln\gamma_i = G_M^{XS} + \left(1 - C_i\right)\left(\frac{\partial G_M^{XS}}{\partial C_i}\right) \tag{2}$$

Equations (1) and (2) provide

$$\ln\gamma_A = C_B^2\left[a_1 - a_2 + 2C_Ba_2 + C_A\left(3C_B - 1\right)a_3 + 2C_AC_B\left(2C_B - 1\right)a_4\right] \tag{3}$$

$$\ln\gamma_B = C_A^2\left[a_1 + 2C_Ba_2 + C_B\left(2 - 3C_B\right)a_3 + C_B^2\left(3 - 4C_B\right)a_4\right] \tag{4}$$

The Equations (3) and (4) are utilized to ascertain the values of the activity coefficient of the components A and B respectively.

The activity coefficient, γ_i and activity, $a_i\left(i = A, B\right)$ of a binary melt are related as [5]

$$\Upsilon_i = \frac{a_i}{C_i} \tag{5}$$

The excess entropy, S_i^{XS} for i^{th} component $\left(i \equiv A, B\right)$ of a binary melt is represented by [9]

$$\frac{S_i^{XS}}{R} = -\ln\gamma_i - T\left(\frac{\partial \ln\gamma_i}{\partial T}\right)_P \tag{6}$$

The Equations (3), (4) and (6) yield

$$\begin{aligned}\frac{S_A^{XS}}{R} = -C_B^2\Big[&\left(a_1 + a_1'T\right) + \left(2C_B - 1\right)\left(a_2 + a_2'T\right)\\ &+ \left(1 - C_B\right)\left(3C_B - 1\right)\left(a_3 + a_3'T\right)\\ &+ 2C_B\left(1 - C_B\right)\left(2C_B - 1\right)\left(a_4 + a_4'T\right)\Big]\end{aligned} \tag{7a}$$

$$\begin{aligned}\frac{S_B^{XS}}{R} = -C_A^2\Big[&\left(a_1 + a_1'T\right) + 2C_B\left(a_2 + a_2'T\right)\\ &+ C_B\left(2 - 3C_B\right)\left(a_3 + a_3'T\right) + C_B^2\left(3 - 4C_B\right)\left(a_4 + a_4'T\right)\Big]\end{aligned} \tag{7b}$$

where, a prime on $a_j\left(j = 1,2,3,4\right)$ refers to the temperature derivative of interaction parameters *i.e.* $\frac{\partial a_j}{\partial T}\left(i \equiv 1,2,3,4\right)$.

The excess entropy of mixing, S_M^{XS} for a binary solution is expressed as [5] [9]

$$\frac{S_M^{XS}}{R} = C_A\frac{S_A^{XS}}{R} + C_B\frac{S_B^{XS}}{R} \tag{8}$$

The above equation can be used to compute S_M^{XS} of a binary melt.

Now the entropy of mixing, S_M for the binary solution may be represented by [5]

$$\frac{S_M}{R} = \frac{S_M^{XS}}{R} + \frac{S_M^{id}}{R}$$

$$\frac{S_M}{R} = \frac{S_M^{XS}}{R} - \left(C_A\ln C_A + C_B\ln C_B\right) \tag{9}$$

The Equation (9) represents the analytical expression for the computation of S_M of a binary melt.

The heat of mixing, H_M of a binary melt may be expressed as [5]

$$H_M = G_M^{XS} - T\left[\frac{\partial G_M^{XS}}{\partial T}\right] \tag{10}$$

Equations (1) and (10) provide

$$\frac{H_M}{RT} = TC_AC_B\left[a_1' + C_Ba_2' + C_AC_Ba_3' + C_AC_B^2a_4'\right] \tag{11}$$

The H_M for a binary solution can also be expressed as [5]

$$\frac{H_M}{RT} = \frac{G_M}{RT} + \frac{S_M}{R} \tag{12}$$

where, G_M stands for Gibbs free energy of mixing of a binary melt.

The microscopic function like $S_{cc}\left(0\right)$ [18] [19] is an important parameter to describe the nature of atomic interactions existing in a binary melt. For segregation, $S_{cc}\left(0\right) > S_{cc}^{id}\left(0\right)$ which causes due to like atoms (A-A or B-B) interactions in the molten system. Similarly for ordering character, $S_{cc}\left(0\right) < S_{cc}^{id}\left(0\right)$ which is an indication of unlike atoms (A-B) interactions persisting in the binary melt [5].

The expression for $S_{cc}(0)$ may be expressed as [5] [18]

$$S_{cc}(0) = RT\left[\frac{\partial G_M}{\partial c^2}\right]^{-1}_{T,P,N} \tag{13}$$

where, G_M can be expressed as

$$G_M = G_M^{XS} + G_M^{id}$$

$$G_M = G_M^{XS} + RT\left[C_A \ln C_A + C_A \ln C_A\right]$$

$$\frac{G_M}{RT} = \frac{G_M^{XS}}{RT} + \left[C_A \ln C_A + C_A \ln C_A\right]$$

$$\frac{G_M}{RT} = C_A C_B\left[a_1 + C_B a_2 + C_A C_B a_3 + C_A C_B^2 a_4\right] + \left(C_A \ln C_A + C_B \ln C_B\right) \text{ (from Equation (1))} \tag{14}$$

Equations (13) and (14) provide

$$\begin{aligned} S_{cc}(0) = \Bigg[& -2a_1 + 2\left(3C_A - 2\right)a_2 + 2\left(1 - 6C_A + 6C_A^2\right)a_3 \\ & + 2\left(1 - 9C_A + 18C_A^2 - 10C_A^3\right)a_4 + \frac{1}{C_A C_B}\Bigg]^{-1} \end{aligned} \tag{15}$$

The $S_{CC}(0)$ in terms of activity can also be represented as [4] [18]

$$S_{cc}(0) = C_B a_A\left[\frac{\partial a_A}{\partial C_A}\right]^{-1}_{T,N,P} = C_A a_B\left[\frac{\partial a_B}{\partial C_B}\right]^{-1}_{T,N,P} \tag{16}$$

The values of $S_{CC}(0)$ determined from expression (16) are generally regarded as the experimental data [5] [18].

For ideal binary melt, $a_j\left(j = 1,2,3,4\right) = 0$ hence Equation (15) reduces to

$$S_{CC}^{id}(0) = C_A C_B \tag{17}$$

where, $S_{CC}^{id}(0)$ represents the ideal value of $S_{CC}(0)$.

The microscopic function such as SRO, α_1 [20], [21] describes the arrangement of atoms in a binary melt. The negative value of α_1 stands for the ordering character of the binary melt whereas the positive value of α_1 illustrates the segregating behavior of the binary melt and $\alpha_1 = 0$ denotes the random distribution in the mixture [5].

In terms of $S_{CC}(0)$, α_1 is represented as [5] [19]

$$\alpha_1 = \frac{S-1}{S\left(Z-1\right)+1} \quad \text{with,} \quad S = \frac{S_{cc}(0)}{S_{cc}^{id}(0)} \tag{18}$$

where, Z = coordination number which is usually assumed to be 10 during computation.

The excess stability function, E^{XS} introduced by Darken [22] is directly related to $S_{CC}(0)$ as [5] [18]

$$\frac{E^{XS}}{RT} = \frac{1}{S_{CC}(0)} - \frac{1}{S_{CC}^{id}(0)} \tag{19}$$

It is evident that $S_{CC}(0) > S_{CC}^{id}(0)$ corresponds to $\frac{E^{XS}}{RT} < 0$ for segregating alloys whereas $S_{CC}(0) < S_{CC}^{id}(0)$ exhibits $\frac{E^{XS}}{RT} > 0$ for ordered alloys and $S_{CC}(0) = S_{CC}^{id}(0)$ refers to $\frac{E^{XS}}{RT} = 0$ for ideal solution [5].

2.2. Surface Properties of the Binary Melts at a Given Temperature

The surface tension is one of the important properties to describe the mechanical behavior of binary solution. For this, Butler model [11] has been utilized in conjunction with FPM to investigate the surface properties like C_i^s and σ of the binary melts.

In the framework of Butler model [11], σ of a binary melt may be expressed as

$$\sigma = \sigma_A + \left[\frac{\tilde{G}_A^{E,s} - \tilde{G}_A^{E,b}}{S_A}\right] + \frac{RT}{S_A}\ln\left[\frac{\ln C_A^S}{C_A}\right] \tag{20a}$$

$$\sigma = \sigma_B + \left[\frac{\tilde{G}_B^{E,s} - \tilde{G}_B^{E,b}}{S_B}\right] + \frac{RT}{S_B}\ln\left[\frac{\ln C_B^S}{C_B}\right] \tag{20b}$$

where, $\sigma_i\left(i = A, B\right)$ = surface tension of pure component, *i*, $\tilde{G}_i^{E,s}$ and $\tilde{G}_i^{E,b}$ $\left(i \equiv A, B\right)$ = partial excess free energies of the component, *i* at the surface and in the bulk respectively, $S_i\left(i \equiv A, B\right)$ = molar surface area of the i^{th} component, C_i^s and $C_i\left(i \equiv A, B\right)$ = surface and bulk concentrations respectively. The expression for $S_i\left(i \equiv A, B\right)$ is represented as [5] [15]

$$S_i\left(i \equiv A, B\right) = 1.09 V_i^{\frac{2}{3}} N_A^{\frac{1}{3}} \tag{21}$$

where, N_A = Avogadro's number and V_i = atomic volume of the ith component.

Now, $\gamma_i\left(i \equiv A, B\right)$ and $\tilde{G}_i^{E,b}$ are related as [5],

$$\tilde{G}_i^{E,b} = RT\ln\gamma_i \tag{22}$$

Again, the relation between $\tilde{G}_i^{E,s}$ and $\tilde{G}_i^{E,b}\left(i \equiv A, B\right)$ is [5] [16]

$$\tilde{G}_i^{E,s} = \lambda \tilde{G}_i^{E,b} \tag{23}$$

with, $\lambda = \frac{Z^s}{Z}$ [23] [24] whose value lies between 0.50 to 0.84 [25] where, Z and Z^s = surface coordination number and bulk coordination number respectively.

2.3. Transport Properties of a Binary Melt at Given Temperature

The diffusion coefficient, D and viscosity, η play a vital role to investigate microscopically the mixing properties of a binary solution. In terms of $S_{cc}(0)$, the diffusivity ratio, $\frac{D_M}{D_{id}}$ for a binary system [5], [15] is given by

$$\frac{D_M}{D_{id}} = \frac{S_{cc}^{id}(0)}{S_{cc}(0)} \tag{24}$$

where, D_M = mutual diffusion coefficient of the mixture, and D_{id} = intrinsic diffusion coefficient *i.e.*

$$D_{id} = C_A D_B + C_B D_A \tag{25}$$

where, $D_i\,(i = A, B)$ stands for self-diffusion coefficients of pure i^{th} component. Equation (24) indicates that for the segregating alloys $D_M < D_{id}$ because $S_{cc}(0) > S_{cc}^{id}(0)$ whereas for ordered alloys $D_M > D_{id}$ because $S_{cc}(0) < S_{cc}^{id}(0)$ [5].

In the substructure of Moelwyn-Hughes approach [12], the viscosity of a simple binary system is represented as [5] [15]

$$\eta = \eta_{id}\left[1 - \left(2\frac{H_M}{RT}\right)\right] \tag{26}$$

$$\text{with,}\quad \eta_{id} = C_A\eta_A + C_B\eta_B \tag{27}$$

where, η_A and η_B = viscosities of pure elements A and B respectively, η_{id} = viscosity of ideal binary mixture.

Equations (26) and (27) yield

$$\eta = \left(C_A\eta_A + C_B\eta_B\right)\left(1 - 2\frac{H_M}{RT}\right) \tag{28}$$

The above equation is utilized to determine the concentration dependency of the viscosity of a binary solution.

3. Results and Discussions

3.1. Thermodynamic and Microscopic Behavior of Zn-Cd Melts at 800 K

The analytical Equations deduced in the substructure of FPM are used to assess the various thermodynamic and microscopic functions relative to the concentration of Zn for Zn-Cd melts at 800 K. The essential interaction parameters a_1, a_2, a_3 and a_4 are evaluated which are used to compute the various properties of Zn-Cd melts at 800 K. For the assessment of the model parameters, Equation (1) is utilized on using the experimental data of G_M^{XS} for Zn-Cd melts at 800 K [1]. Initially, the experimental values of activity coefficients in infinite dilute solution range for Zn-Cd melts at 800 K *i.e.* $\gamma_{Zn} = 3.304$ and $\gamma_{Cd} = 4.154$ [1] are utilized to reckon the values of a_1 and a_2 form the expressions shown below [9]

$$a_1 = \ln\gamma_{Cd}^0(Zn) = \frac{1}{RT}\ln\left[\frac{\partial G_M^{XS}}{\partial C_B}\right]_{C_A\to 1.0} \tag{29a}$$

$$a_2 = \ln\gamma_{Zn}^0(Cd) - \ln\gamma_{Cd}^0(Zn) \tag{29b}$$

$$\text{with,}\quad \ln\gamma_{Zn}^0(Cd) = a_1 + a_2 = \frac{1}{RT}\left[\frac{\partial G_M^{XS}}{\partial C_A}\right]_{C_B\to 1.0} \tag{30}$$

It should be mentioned that for the estimation of model parameters for regular associated solution model [9] [26], the infinite dilute solution range data of activity coefficients are also used. The values of a_1 and a_2 are found to be 1.424072 and -0.228938 respectively which are regarded as the starting values of a_1 and a_2. Again, for the evaluation of a_3 and a_4, the successive approximation method [14], [15] is utilized on using the experimental data of G_M^{XS} for Zn-Cd melts at 800 K in the relation given below.

$$\frac{G_M^{XS}}{RT}\frac{1}{C_A C_B} - a_1 - a_2 C_B = C_A C_B a_3 + C_A C_B^2 a_4 \quad \text{(from Equation (1))} \tag{31}$$

It is necessary to note that the values of a_3 and a_4 are not determined as suggested in the literature [9]. The values of a_1, a_2, a_3 and a_4 are slightly adjusted to achieve a well agreement between the theory and experiment [1] for G_M^{XS} of Zn-Cd melts at 800 K. The best fit values are

$$a_1 = 1.4116, \quad a_2 = -0.2228, \quad a_3 = -0.6556 \quad \text{and} \quad a_4 = 0.4917$$

Now, the above values of the model parameters are employed in Equations (1) and (14) to estimate the theoretical values for $\frac{G_M^{XS}}{RT}$ and $\frac{G_M}{RT}$ of Zn-Cd melts at 800 K as a function of composition. **Figure 1** shows excellent harmony between the theoretical results and the correlated experimental data [1] for both $\frac{G_M^{XS}}{RT}$ and $\frac{G_M}{RT}$ of Zn-Cd melts at 800 K.

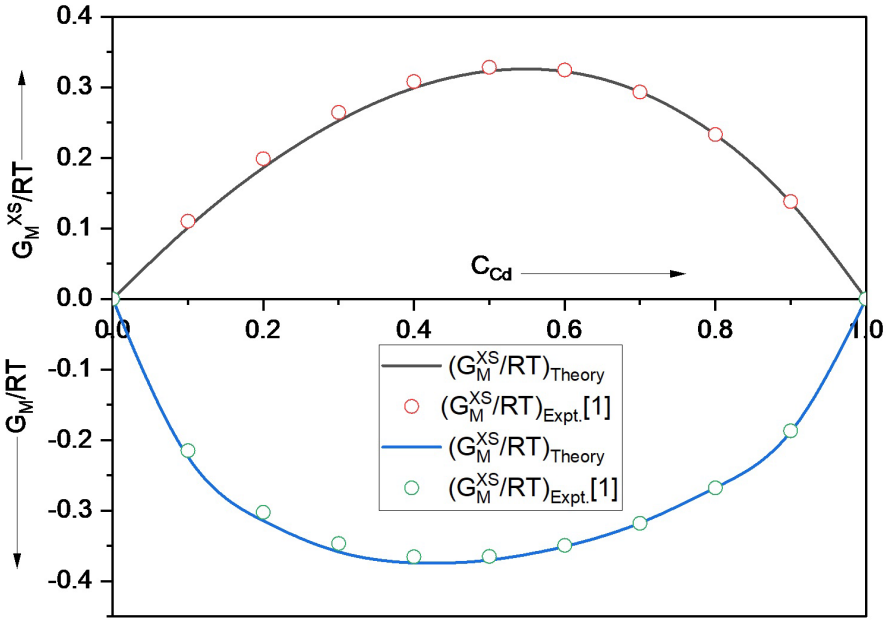


Figure 1. $\frac{G_M^{XS}}{RT}$ and $\frac{G_M}{RT}$ versus C_{Zn} for Zn-Cd melts at 800 K.

The values of $\frac{G_M^{XS}}{RT}$ are found to be positive in the entire concentration range

having maximum values at $C_{Zn} = 0.5$ i.e 0.3005 (Theory) and 0.3008 (Experiment). The positive values of $\frac{G_M^{XS}}{RT}$ indicate the segregating character of Zn-Cd melts at 800 K. Again, the symmetry in $\frac{G_M^{XS}}{RT}$ for Zn-Cd melts at 800 K is well explained.

The $\frac{G_M}{RT} - C$ isotherms illustrate the minimum values of $\frac{G_M}{RT}$ at $C_{Zn} = 0.5$. *i.e.* – 0.3926 (Theory) and – 0.3927 (Experiment). The reported minimum value of $\frac{G_M}{RT}$ is found to be - 0.3864 at $C_{Zn} = 0.5$ for Cd-Zn melts at 800 K [6]. Thus, the observed symmetry in $\frac{G_M}{RT}$ is successfully explained by the present theoretical model. Farther, the magnitude of $\frac{G_M}{RT}$ refers to the weakly interacting nature of Zn-Cd melts at 800 K [18].

The theoretical results for γ_{Zn} and γ_{Cd} for Zn-Cd melts at 800 K exhibit well agreement with the correlated experimental data [1] as depicted in **Figure 2**. The theoretical values of γ_{Zn} and γ_{Cd} are utilized to compute the values of a_{Zn} and a_{Cd} respectively from Equations (3) and (4) for Zn-Cd system at 800 K relative to Zn-composition which are cited in **Figure 3** together with the correlated experimental data [1]. A well agreement is noticed between the theory and experiment. Obviously, a_{Zn} and a_{Cd} indicate positive deviations from the linearity in the whole concentration range of Cd which refers to the segregating nature of Zn-Cd molten system at 800 K. The agreement between the theory and experiment of a_{Zn} and a_{Cd} validates the values of a_1, a_2, a_3 and a_4.

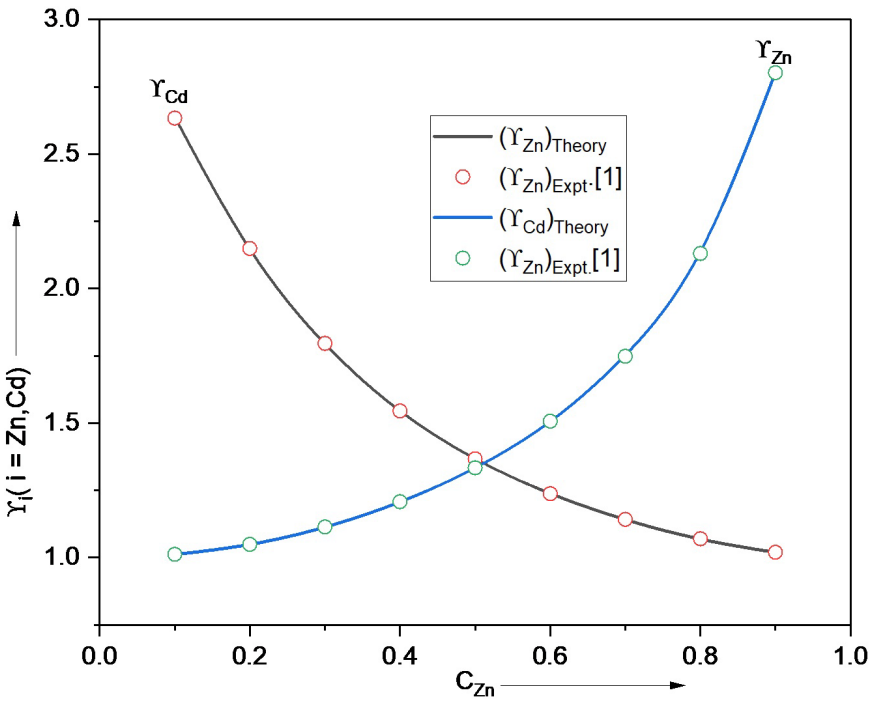


Figure 2. $\gamma_i \left(i = Zn, Cd\right)$ versus C_{Zn} for Zn-Cd melts at 800 K.

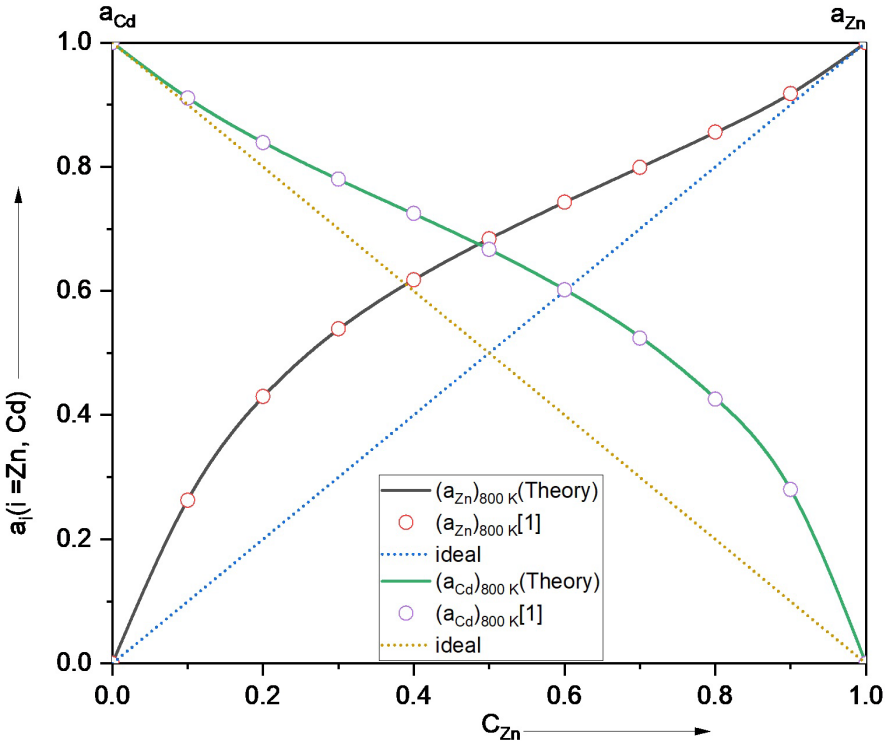


Figure 3. $a_i\ (i = Zn, Cd)$ versus C_{Zn} for Zn-Cd melts at 800 K.

For the calculations of S_M^{XS} from Equation (8) on employing Equation (7a) and (7b), the temperature derivative of interaction parameter $\frac{\partial a_j}{\partial T}(j = 1,2,3,4)$ are required. The values of the temperature derivative of interaction parameters are evaluated by least square method on employing the experimental data of H_M [1] for Zn-Cd melts at 800 K in Equation (11). The estimated values are

$$\frac{\partial a_1}{\partial T} = 1.73\times10^{-4}\ \mathrm{K}^{-1},\ \frac{\partial a_2}{\partial T} = 1.6\times10^{-6}\ \mathrm{K}^{-1},\ \frac{\partial a_3}{\partial T} = -1.4928.03\times10^{-6}\ \mathrm{K}^{-1},$$

$$\frac{\partial a_4}{\partial T} = -2.05\times10^{-5}\ \mathrm{K}^{-1}$$

The above values of $\frac{\partial a_j}{\partial T}(j = 1,2,3,4)$ are utilized to compute the concentration dependence of S_M^{XS}, S_M and H_M of Zn-Cd melts at 800 K.

Now, the theoretical results for $\frac{S_M^{XS}}{R}$ on using Equations (7a), (7b) and (8) are compared with the experimental data [1] of Zn-Cd melts at 800 K in **Figure 4**. A reasonable agreement is noticed having a maximum error of 5.30% at $C_{Zn} = 0.5$.

Figure 5 represents the compassion between the theoretical values of $\frac{S_M}{R}$ computed from Equation (9) and the experimental data [1] of Zn-Cd system at 800 K. An excellent agreement is observed. Obviously, $\frac{S_M}{R}$ denotes the positive values in the entire composition range of Zn with maxima at $C_{Zn} = 0.5$ *i.e.*

0.7073 (Theory) and 0.7049 (Experiment). Therefore, the observed symmetry in S_M for Zn-Cd melts at 800 K is explained theoretically.

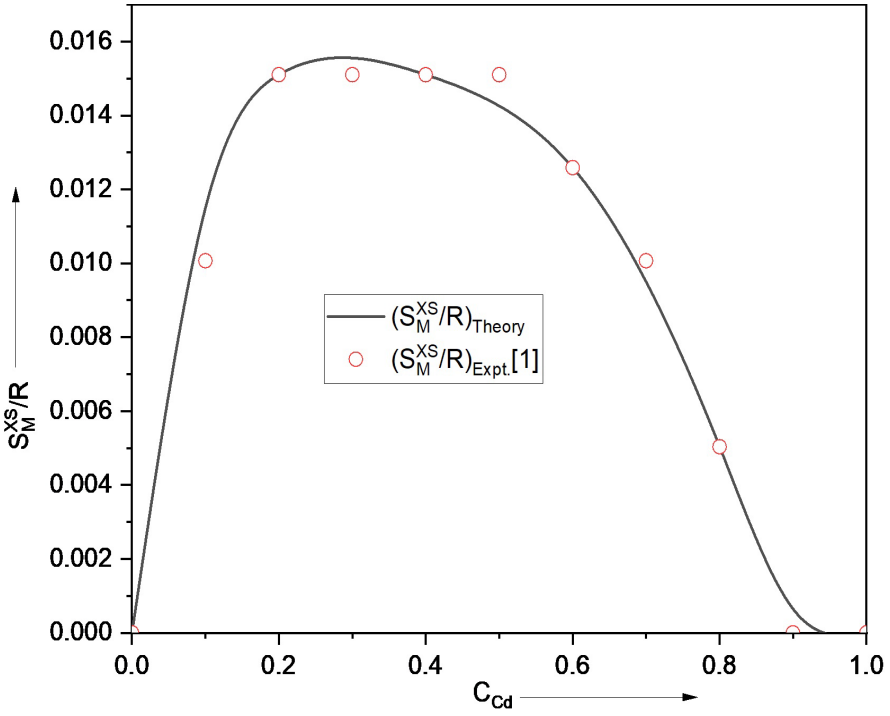


Figure 4. $\frac{S_M^{XS}}{R}$ versus C_{Zn} for Zn-Cd melts at 800 K.

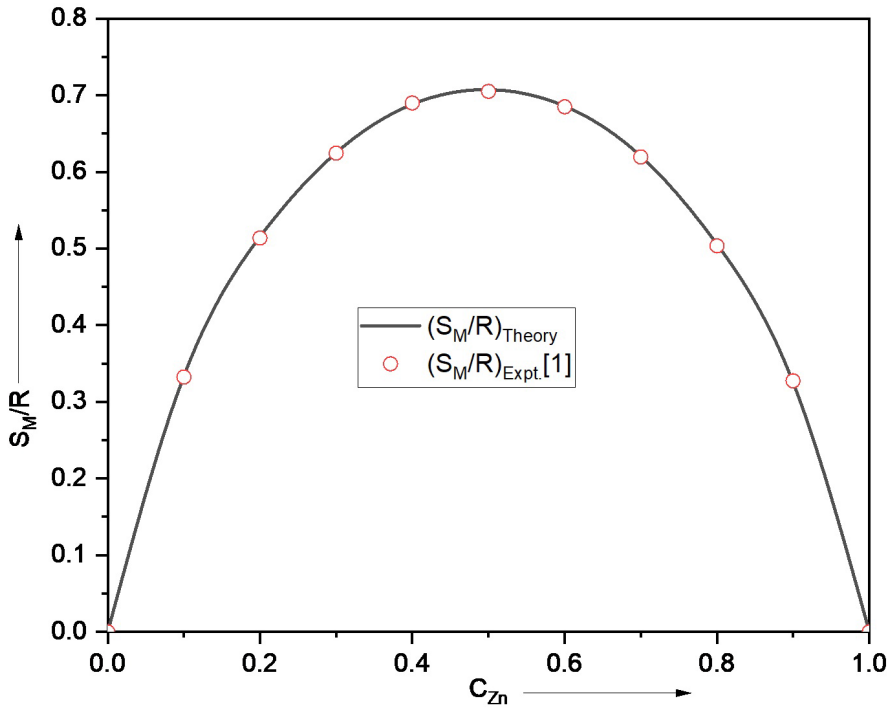


Figure 5. $\frac{S_M}{R}$ versus C_{Zn} for Zn-Cd melts at 800 K.

The comparison between the theoretical results of $\frac{H_M}{RT}$ calculated from Equation (12) with the experimental results [1] for Zn-Cd melts at 800 K is illustrated in **Figure 6**. A well harmony has been found between theory and experiment. In the concentration range, $C_{Zn}=0.1$ to 0.9, $\frac{H_M}{RT}$ exhibits positive values having maxima at $C_{Zn}=0.5$ *i.e.* 0.3148 both (Theory and Experiment). Hence, the symmetric nature of H_M for Zn-Cd system at 800 K is successfully reproduced. Again, the sign and magnitude of the values of $\frac{H_M}{RT}$ indicate that Zn-Cd melt at 800 K is a feebly segregating alloy [5].

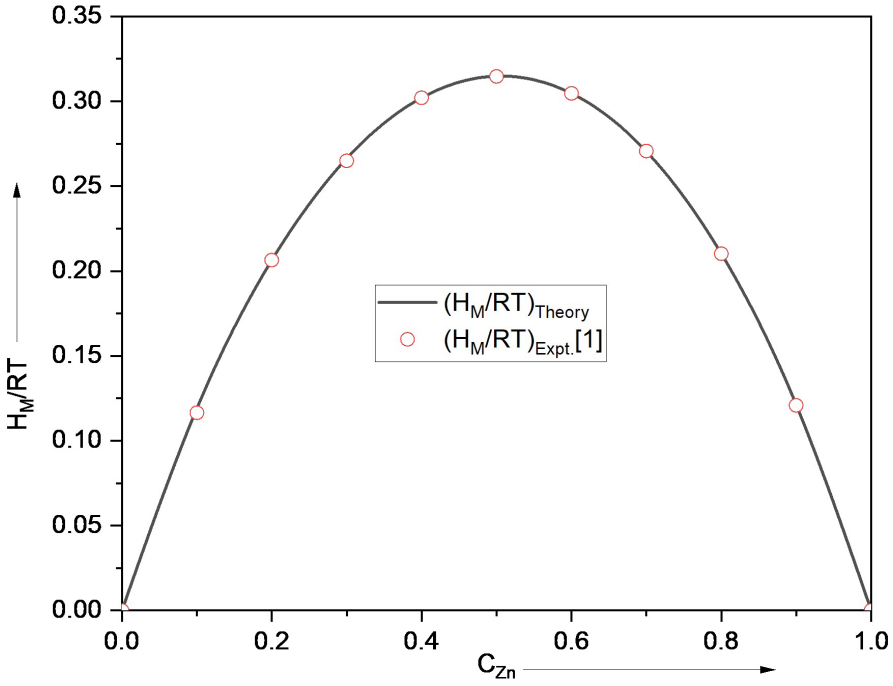


Figure 6. $\frac{H_M}{RT}$ versus C_{Zn} for Zn-Cd melts at 800 K.

Figure 6 exhibits the concentration dependence of $S_{CC}(0)$ for Zn-Cd melts at 800 K ascertained from Equation (15) relative to the concentration of Zn. The experimental data [1] and $S_{cc}^{id}(0)$ are also included in **Figure 6**. It is evident that the theoretical results agree well with the experimental results having maxima *i.e.* 0.555 (both theory and Experiment) at $C_{Zn}=0.5$. Again, in the entire composition range of Zn, $S_{cc}(0)>S_{cc}^{is}(0)$ which is a sign of segregating nature of Zn-Cd melts at 800 K.

The concentration dependence of α_1 determined from Equation (18) for Zn-Cd melts at 800 K is also presented in **Figure 7**. It should be pointed out the no experimental data of α_1 is available in the literature for comparison. From **Figure 7**, it is clear that α_1 is positive at each concentration in the region, $C_{Zn}=0.1$ to 0.9 with a maximum value of 0.0582 at $C_{Zn}=0.5$ which indicates the weakly segregating character of Zn-Cd melts at 800 K [5].

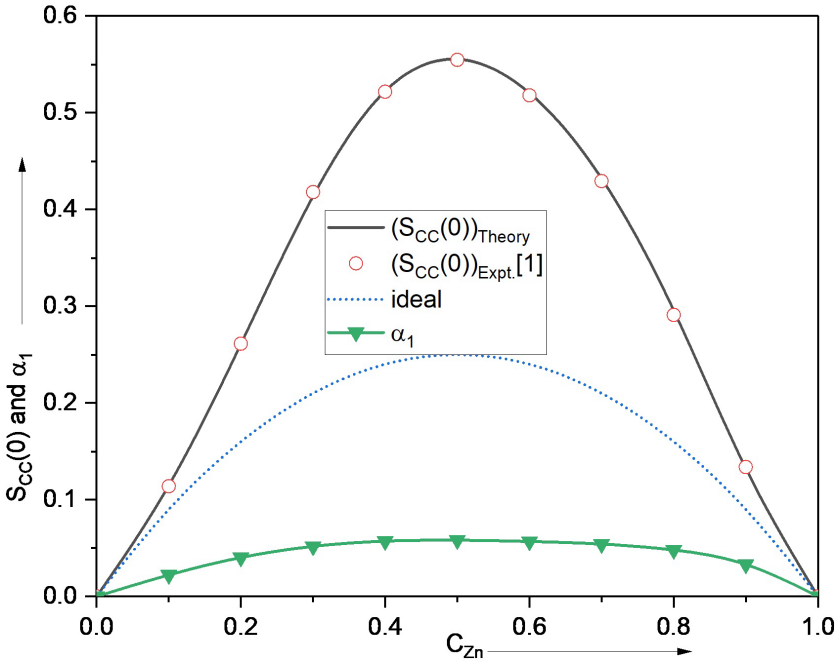


Figure 7. $S_{CC}(0)$ and α_1 versus C_{Zn} for Zn-Cd melts at 800 K.

The Equation (19) is utilized to determine the theoretical values of $\frac{E^{XS}}{RT}$ for Zn-Cd melts at 800 K as a function of the composition of Zn. The $\frac{E^{XS}}{RT}-C$ isotherm cited in **Figure 8**, indicates that Zn-Cd melts at 800 K is a feebly segregating alloy [5].

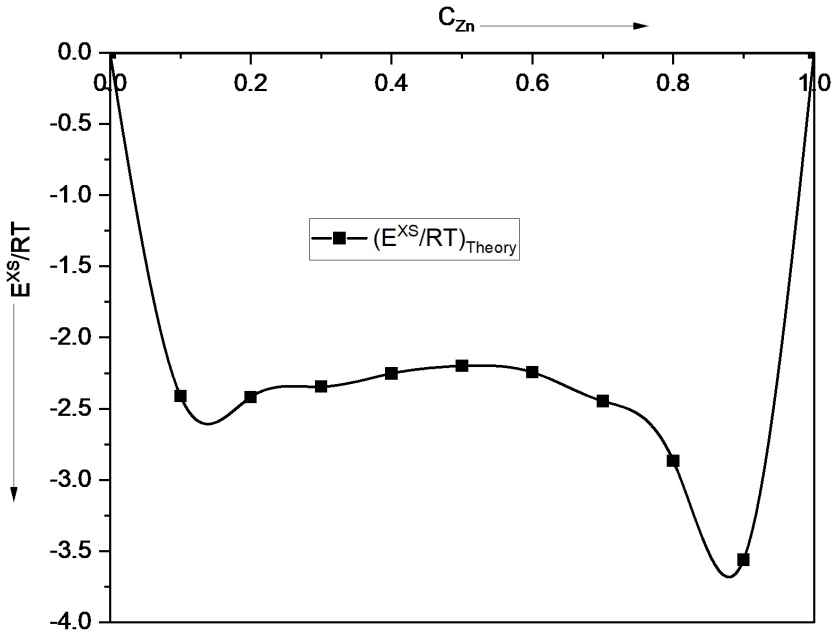


Figure 8. $\frac{E^{XS}}{RT}$ versus C_{Zn} for Zn-Cd melts at 800 K.

3.2. Surface Properties of Zn-Cd System at 800 K

The surface tension, σ for Zn-Cd molten system can be determined on using equations (20a) and (20b) respectively. In order to determine the value of σ, the values of $\tilde{G}_i^{E,b}$, $\tilde{G}_i^{E,s}$, S_i and $C_i^s\left(i \equiv Zn, Cd\right)$ are essential. The values of $\tilde{G}_i^{E,b}$ are determined for the compositions, C_{Zn} = 0.1. 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 using equation (22) on employing the theoretical values of activity coefficient, $\gamma_i\left(i \equiv Zn, Cd\right)$ for Zn-Cd liquid alloys at 800 K. The values of $\tilde{G}_i^{E,s}\left(i \equiv Zn, Cd\right)$ are computed from Equation (23) on taking $\lambda = 0.82$ [27]. For the computations of S_i, $V_i\left(i \equiv Zn, Cd\right)$ is required which is obtained from the relation

$$V_i\left(T\right) = \frac{M_i}{\rho_i\left(T\right)} \tag{32a}$$

$$\text{with} \quad \rho_i\left(T\right) = \rho_i\left(T_m\right) + \frac{\partial \rho_i}{\partial T}\left(T - T_m\right) \tag{32b}$$

where, T = 800 K, T_m = the melting temperature of the component, i, M_i = the atomic mass of component i, $\rho_i\left(T_m\right)$ and $\rho_i\left(T\right)$ = densities of the i^{th} components at the melting temperature and required temperatures respectively, and $\frac{\partial \rho_i}{\partial T}$ = the temperature coefficient of density for i^{th} component . The necessary input data is mentioned in **Table 1** [28].

Table 1. The physical properties of Zn and Cd [28].

Metal	Metal	M.P.	Atomic mass	Density
	(in K)	M (in Kg)	ρ (in Kgm^{-3})	$\frac{\partial \rho}{\partial T}$ (in $Kgm^{-3}K^{-1}$)
Zn	692.62	0.03538	6580	−0.98
Cd	594.05	0.11241	8010	−1.22

The values of σ for pure Zn and Cd at 800 K aredetermined from relation

$$\sigma_i\left(T\right) = \sigma_i\left(T_m\right) + \frac{\partial \sigma_i}{\partial T}\left(T - T_m\right) \tag{33}$$

where,

$\frac{\partial \sigma_i}{\partial T}$ = temperature coefficient of surface tension of the i[th] component

The required properties for pure Zn and Cd are given in **Table 2**.

Table 2. Surface tension and surface coefficient of surface tension for Zn and Cd [28].

Metal	Surface tension	Coefficient of surface tension
	(σ in $mN{\cdot}m^{-1}$)	($\frac{\partial \sigma}{\partial T}$ in $mN{\cdot}m^{-1}{\cdot}K^{-1}$)
Zn	782	−0.17
Cd	570	−0.26

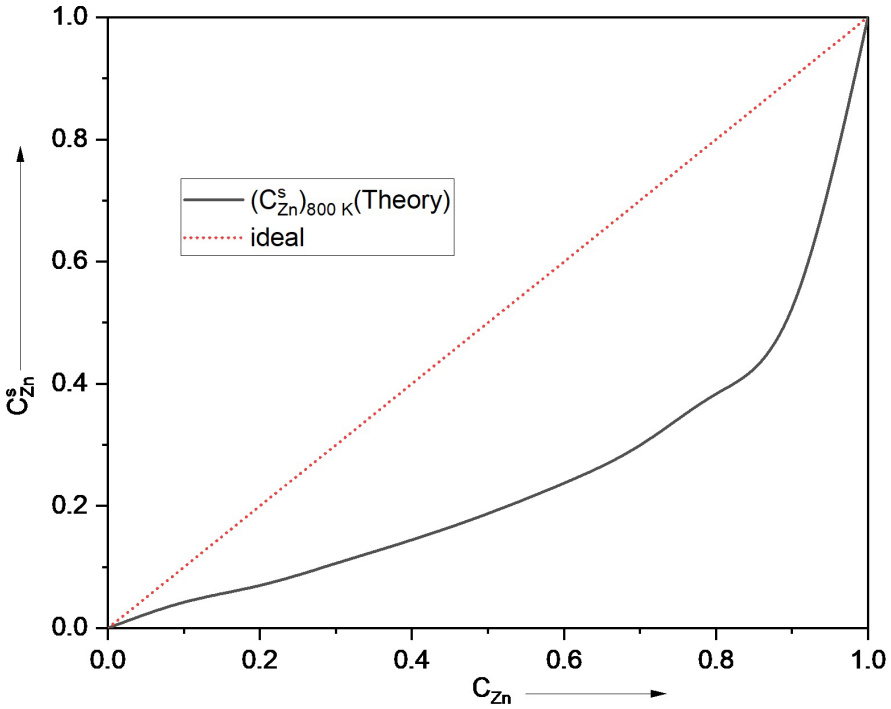


Figure 9. C^s_{Zn} versus C_{Zn} for Zn-Cd melts at 800 K.

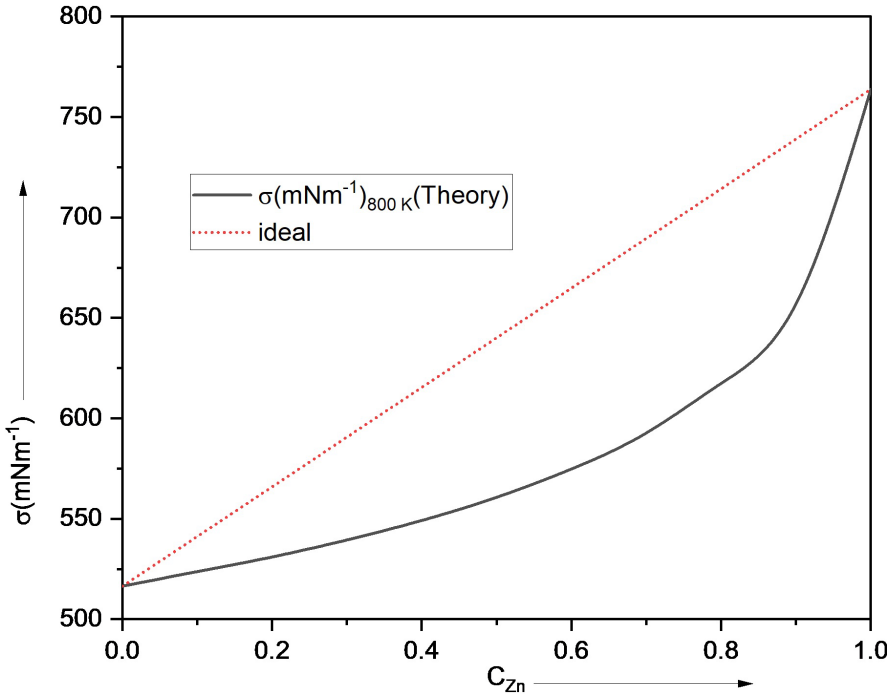


Figure 10. σ versus C_{Zn} for Zn-Cd melts at 800 K.

The values of the partial excess free energy for Zn and Cd melts in the bulk and at the surface are determined from Equations (22) and (23) at 800 K.

The Equations (20a) and (20b) are solved simultaneously to compute the values of C^s_{Zn} and σ for Zn-Cd melts at 800 K relative to the bulk concentration of

Zn *i.e.* $C_{Zn}^{b} = C_{Zn}$. The concentration dependency of C_{Zn}^{s} at 800 K for Zn-Cd melts cited in Figure 9. Obviously, C_{Zn}^{s} denotes the negative deviation from linearity with the increase in the bulk concertation of Zn which advocates the excess number of atoms of Cd at the surface.

The theoretical values of σ as a function of bulk concentration of Zn for Zn-Cd melts at 800 K are illustrated in Figure 10. The $\sigma - C_{Zn}$ isotherm indicates the elevation of the surface tension of Zn-Cd melts at 800 K with the increase in the bulk composition of Zn because the surface tension of pure Zn is more than that of pure Cd.

3.3. Transport Properties of Zn-Cd System at 800 K

The concentration dependency of $\frac{D_M}{D_{id}}$ for Zn-Cd melts at 800 K evaluated from Equation (24), has been illustrated in Figure 11. It is evident that $\frac{D_M}{D_{id}} < 1$ in the entire concentration range, $C_{Zn} = 0.1$ to 0.9 which shows the segregating character of Zn-Cd melts at 800 K and the maximum possibility of segregation is at $C_{Zn} = 0.5$ due to the minimum value of $\frac{D_M}{D_{id}} = 0.450$ [4] [15]. Again, the magnitude of $\frac{D_M}{D_{id}}$ corresponds to the weakly segregating nature of Zn-Cd melts at 800 K.

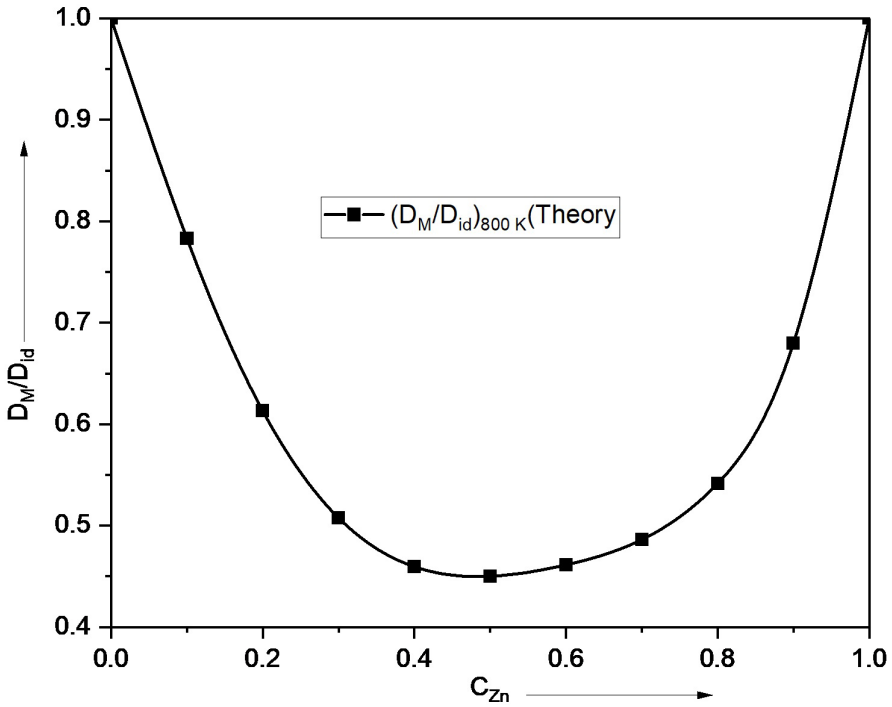


Figure 11. $\frac{D_M}{D_{id}}$ versus C_{Zn} for Zn-Cd melts at 800 K.

For the computation of η for Zn-Cd melts at 800 K from Equation (28), the values of the viscosity of pure Zn and pure Cd are required which are available in

the literature [29].

The theoretical values of η obtained from Equation (28) for Zn-Cd melt at 800 K are cited in **Figure 12**. The $\eta - C_{Zn}$ isotherm deviates negatively from linearity in the whole Zn-composition range. The value of η at first gradually degrades to a minimum value of 0.8228 (mPa S) $C_{Zn} = 0.5$ and then increases with the addition of Zn-Component in Zn-Cd liquid alloys at 800 K. This is a sign of the probability of maximum segregation at $C_{Zn} = 0.5$ in Zn-Cd melts at 800 K [5]. Again, the magnitude of η signifies that molten Zn-Cd alloy at 800 K is a feebly segregating system. It should be pointed out that the experimental results for η of Zn-Cd melts at 800 K are not available in the literature for comparative study.

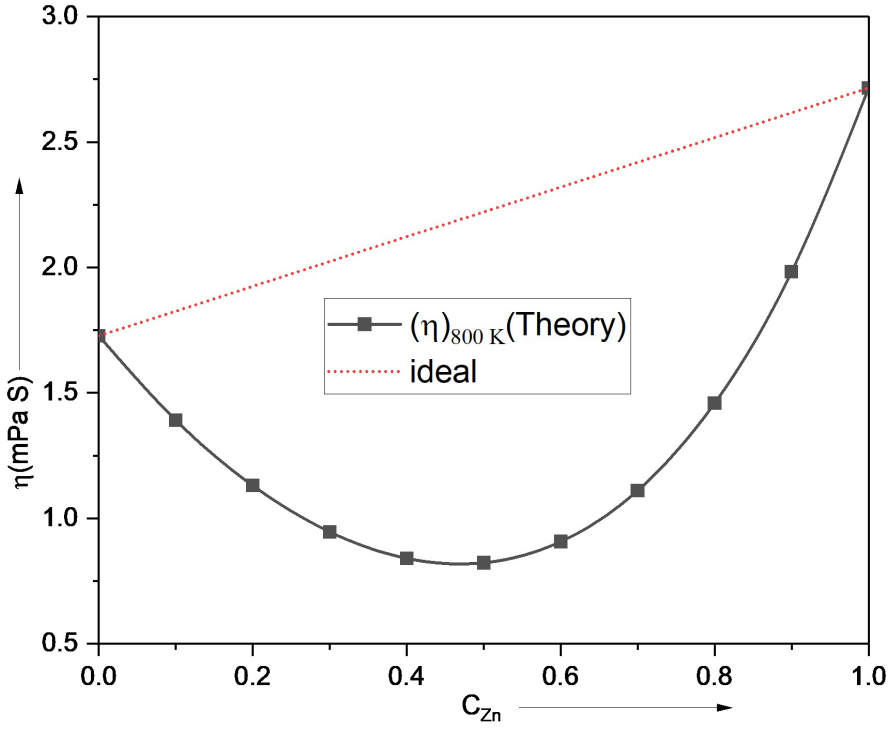


Figure 12. η versus C_{Zn} for Zn-Cd melts at 800 K.

4. Conclusions

The present theoretical investigation successfully explains the observed symmetries in G_M^{XS}, G_M, S_M and H_M for Zn-Cd liquid alloys at 800 K. The positive departures of a_{Zn} and a_{Cd} from linearity, $S_{cc}(0) > S_{cc}^{id}(0)$, positive value of α_1 and $\frac{D_M}{D_{id}} < 1$ indicate that Zn-Cd melt at 800 K is a feebly segregating system. The C_{Zn}^s exhibits negative deviation from the linearity with respect to the bulk concentration of Zn which indicates that Cd is enriched at the surface relative to the bulk. Again, the $\sigma - C$ isotherm shows that the surface tension of Zn-Cd melts at 800 K increases with the addition of Zn-atoms in the melt. Further,

$\eta - C$ isotherm indicates that η is minimum for Zn-Cd melts at 800 K about $C_{Zn} = 0.5$ which is an indication of the maximum possibility of the segregation in Zn-Cd melts at 800 K about $C_{Zn} = 0.5$.

Author Contributions

Conceptualization: I.S. Jha and J. Mandal and A.K. Pandey; methodology: R.P. Chaudhary; validation: I.S. Jha; J. Mandal and A.K. Pandey; formal analysis: R.P. Chaudhary; investigation: P.R. Deen and SoniKumari; writing-original draft preparation: P.R. Deen and SoniKumari; writing-review and editing: R.P. Chaudhary; visualization: I.S. Jha and A.K. Pandey; supervision: J. Mandal.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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