Assessment of Mixing Properties of Bi-In liquid alloy at different temperatures

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Abstract

Regular Solution model have been used to describe thermodynamic properties, transport properties and structural properties. The interaction energy is temperature dependent and played an important role to explain the properties of Bi-In liquid alloy at different temperatures. The theoretical values of interchange energy at different temperatures are obtained by best fit parameter approximation with the help of experimental values at 900K. The properties have been studied with the help of computed theoretical interchange energy at different temperatures as all properties of our study in this model is dependent on it. The properties are analyzed on theoretical basis. Comparison of theoretical and experimental values at 900K shows that they are in good agreement.

Keyword - *Regular solution model, order energy parameter, Thermodynamic properties, Transport properties, Structural properties, Different temperatures.*

I. INTRODUCTION

Bi and In are widely used in multi-component lead free solders containing Ag, Sn, Sb and Zn in electronic industry [1-3]. The Bi-In binary alloy is rarely used as a solders, except a few particular compositions. This alloy has crystalline structure and is used as a semiconductor and in photo-optic applications. The alloy also posses superconducting properties [4]. The phase diagram of Bi-In alloy [5] shows that it has three forms of compound i.e. BiIn(β), $BiIn_3$(γ) and $BiIn_2$(δ) among which BiIn alloy has the highest heat of formation and fusion [5, 6]. It is also useful in ternary alloy system : The addition of Sn to the alloy i.e. Bi-In-Sn ternary system has wide range of fusible applications and improves mechanical properties [7]. Likewise,

Zn-based alloys containing Bi-In alloy are used to produce alkaline batteries [2, 5].

The mixing properties of liquid alloys are important for preparation of desired materials. Thermodynamic property is important to understand the behavior of alloys and transport property is required for many metallurgical processes and heterogeneous chemical reactions. In thermodynamic properties we have calculated free energy of mixing (G_M), activity (a), entropy of mixing (S_M) and heat of mixing (H_M). And, in transport properties we have computed viscosity (η) and diffusion coefficient ratio (D_m/D_{id}). Many researchers [8-11] have been working on several models to explain the mixing behavior of binary liquid alloys. We have used regular solution model [12] as the atoms of Bi and In are all alike in shape and size i.e. atomic volume of Bi/atomic volume of In =20.8/16.3 ≈ 1. Thus Bi-In is suitable candidate for investigation using regular solution model. And, viscosity is studied with the help of Moelwyn-Hughes equation [13, 14]. The theoretical formulation has been presented in section (II), result and discussion in section (III) and conclusion in section (IV).

II. FORMALISM

Regular alloys usually have symmetry in free energy of mixing about equiatomic composition and constituent atoms A and B are sufficiently similar in size and shape so they are interchangeable on the lattice. Also, the configurational energy is no longer independent of mutual disposition of two or more kind of atoms. The binary liquid alloy A-B of homogenous solution consists of $C_{A\ (A=Bi)}$ (≡c) mole of A and $C_{B(A=In)}$ {≡(1-c)} mole of B respectively.

A. Thermodynamic properties

The expression for the free energy of mixing (G_M) of binary liquid alloy is

$$G_M = G_M^{id} + G_M^{XS} \quad (1)$$

Where, excess free energy of mixing (G_M^{XS}) and ideal free energy of mixing (G_M^{id}) are given by

$$G_M^{XS} = \omega c_A c_B \quad (2)$$

and

$$G_M^{id} = RT\,[clnc + (1-c)ln(1-c)] \quad (3)$$

From equation (1), (2) and (3), we get

$$G_M = RT\,[c\,ln\,c + (1-c)ln(1-c)] + c(1-c).\omega \quad (4)$$

Where, T stands for temperature, ω is interaction energy and R is molar gas constant.

The expression for activities a_A of the elements A and B (a_B) in the binary liquid alloy can be derived from the standard relations

$$lna_A = lnc + \frac{\omega}{RT}(1-c)^2 \quad (5)$$

and

$$lna_B = \ln(1-c) + \frac{\omega}{RT}c \quad (6)$$

The entropy of mixing (S_M) is given by

$$S_M = -\frac{\partial G_M}{\partial T} \quad (7)$$

From equation (4) and (7), we get

$$\frac{S_M}{R} = -[c\,ln\,c + (1-c)ln(1-c)] - c(1-c).\frac{1}{R}\frac{\partial \omega}{\partial T} \quad (8)$$

The importance of ω as temperature dependent has been studied by Bhatia et. al [15], Ratti and Bhatia [16] , Alblas et. al [17]. The interchange energy (ω) is temperature dependent.

The relation for heat of mixing (H_M) ,entropy of mixing (S_M), and free energy of mixing (G_M) is expressed as

$$\frac{H_M}{RT} = \frac{S_M}{R} + \frac{G_M}{RT} \quad (9)$$

Using equation (4), (8) and (9), we get

$$\frac{H_M}{RT} = c(1-c).\frac{\omega}{RT} + c(1-c)\frac{1}{R}.\frac{\partial \omega}{\partial T} \quad (10)$$

B. Transport Properties

Viscosity and diffusion coefficient are important to study mixing behavior of an alloy in microscopic level. The relation between diffusion coefficient and concentration fluctuation derived by Singh and Sommer [18] is given as

$$\frac{D_M}{D_{id}} = \frac{S_{CC}^{id}(0)}{S_{CC}(0)} \quad (11)$$

Where, D_M is the mutual diffusion coefficient and D_{id} is the intrinsic diffusion coefficient for an ideal mixture calculated as

$$D_M = c_1 D_2 + c_2 D_1 \quad (12)$$

Where, D_1 and D_2 are the self-diffusivities of pure components A and B respectively.

In term of energy order parameter ω, the diffusion coefficient can be expressed as [19]

$$\frac{D_M}{D_{id}} = [1 - \frac{2\omega}{RT}S_{cc}^{id}(0)] \quad (13)$$

We have used the Moelwyn-Hughes equation [13] to investigate the viscosity of Bi-In liquid alloy which is given as

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

Where, η_k (k = 1, 2) is the viscosity of pure component K and can be computed from Arrhenius type equation [20] as

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

Where, η_{0K} 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).

C. Structural Properties

The concentration fluctuation in the long wavelength limit ($S_{cc}(0)$) is used to investigate the nature of atomic order in binary liquid alloy [23] and expressed as,

$$S_{CC}(0) = \frac{RT}{\left(\frac{\partial^2 G_M}{\partial c^2}\right)_{T,P,N}} \quad (16)$$

From equation (4) and (16), we get

$$s_{cc}(0) = \frac{c_A c_B}{1 - 2c_A c_B \cdot \frac{\omega}{RT}} \quad (17)$$

The experimental values of $S_{cc}(0)$ is derived from experimental values of the activities [5] of the constituent species of the binary liquid alloys from the equation

$$s_{cc}(0) = (1-c)a_A\left(\frac{\partial a_A}{\partial c}\right)^{-1}_{T,P,N} = ca_B\left(\frac{\partial a_B}{\partial c}\right)^{-1}_{T,P,N} \quad (18)$$

Where, a_A and a_B are the activities of the component of A and B respectively.

The Warren-Cowley [19, 24] short range order parameter (α_1) is used to study the arrangement of the

atoms in the molten alloys. The theoretical values of these parameters can be evaluated

$$\alpha_1 = \frac{s-1}{s(Z-1)+1} \qquad (19)$$

Here, $= \frac{S_{cc}(0)}{S_{cc}^{id}(0)}$, $s_{cc}^{id}(0) = c_A c_B$

and Z is the coordination number = 10 in our study.

D. Order energy parameter at different temperatures

The values of free energy of mixing (G_M) of the alloy at different temperatures is computed from equation (4) using the values of order energy parameter (ω) at different temperatures from the relation [21, 22]

$$\omega(T) = A + BT \qquad (20)$$

Where, *A* and *B* are coefficient constants.

III. RESULT AND DISCUSSION

The best fit parameters was found to be ω/RT = -1.027 and $\frac{1}{R}\frac{\partial \omega}{\partial T} = -0.048$ at temperature 900k by the method of best fit approximation with the experimental values of the alloy from Hultgren et.al. 1973 [5] using equations (4) and (7).The values of A and B is calculated using the values of ω/RT and $\frac{1}{R}\frac{\partial \omega}{\partial T}$ at temperature 900k of the alloy Bi-In using equation (20). The theoretical values of interchange energy (ω) at different temperatures i.e. 600K, 700K, 800K, 1200K, 1500K, 1800K and 2200K are computed by taking the values of coefficient constants A and B for the alloy which are presented in the table 1.

Table 1
Order energy parameter (ω) at different temperatures

Temperature (T)	Order energy parameter (ω/RT)
600K	-1.5165
700K	-1.3067
800K	-1.1493
900K	-1.0270
1200K	-0.7822
1500K	-0.6354
1800K	-0.5375
2200K	-0.4485

Interaction energy is found to be negative at all temperatures which indicates Bi and In atoms are attracted to each other. We have computed free energy of mixing (G_M), activity (a), entropy of mixing (S_M), heat of mixing (H_M), Ratio of mutual and self-diffusivity (D_M/D_{id}) and viscosity (η) at different temperatures i.e. 600K, 700K, 800K, 1200K, 1500K, 1800K and 2200K) with the help of Regular solution model [12] using theoretically computed interchange energy (ω) presented on table 1.

A. Free energy of mixing

The values of free energy of mixing (G_M) of the alloy at temperatures 600K, 700K, 800K, 1200K, 1500K, 1800K and 2200K have been computed using the values of ω(T) in equation (4) over the entire range of concentration. The free energy of mixing (G_M) of Bi-In liquid alloy at different temperatures of study in the concentration range C_{Bi} = 0.1 to 0.9 is shown in figure (1).

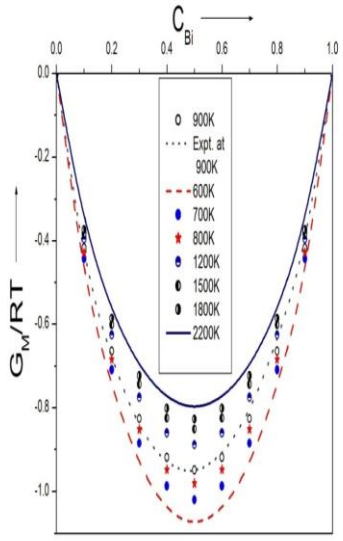

Figure 1. Graph for (G_M/RT) Versus the concentration of C_{Bi} of Bi-In liquid alloy at temperatures 900k, 600K, 700K, 800K, 1200K, 1500K, 1800K and 2200K.

At 900k, the minimum value of G_M/RT at C_{Bi}=0.5 i.e. -0.9499. The theoretical and experimental values [5] of G_M/RT of the alloy are in well agreement at 900K. The values of free energy of mixing are found to be negative in the entire concentration range. And , at temperatures

600K, 700K, 800K, 1200K, 1500K, 1800K and 2200K , the minimum value is at C_{Bi}=0.5 which indicates that the symmetry in free energy of mixing. As the temperature of the alloy increases from 600k to 2200K, the values of G_M/RT increases and vice-versa.

B. Entropy of mixing (S_M)

By best fit method, the theoretical value of $\frac{1}{R}\frac{\partial\omega}{\partial T}$ at 900k is obtained using equation (7) with the help of experimental values of entropy of mixing (S_M) is taken for Hultgren et. al. [5] i.e. $\frac{1}{R}\frac{\partial\omega}{\partial T} = -0.048$. With the help of this theoretical value of $\frac{1}{R}\frac{\partial\omega}{\partial T}$, entropy of mixing is computed at 900K. The entropy of mixing of Bi-In alloy at temperatures 600K, 700K, 800K, 1200K, 1500K, 1800K and 2200K are calculated using equation (7) with the help of values of energy order parameters ω(T) at corresponding temperatures presented on the table 1.

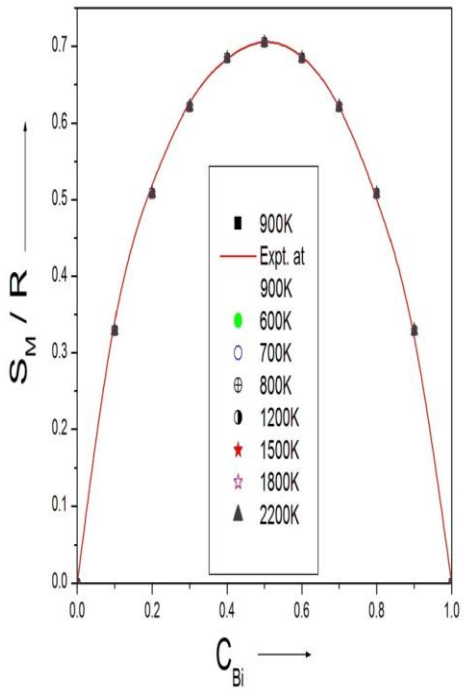

Figure 2. Graph for S_M/R versus the concentration of C_{Bi} of Bi-In liquid alloy at temperatures 900k, 600K, 700K, 800K, 1200K, 1500K, 1800K and 2200K.

The values of S_M/R are found to be positive in the entire concentration range. This explains the symmetry in entropy of mixing of Bi-In liquid alloy at 900k. At our all temperatures of study, the values of entropy of mixing remain unchanged as the theoretical value of $\frac{1}{R}\frac{\partial\omega}{\partial T} = -0.048$ remains constant using equation (20). The maximum theoretical value of S_M/R is 0.4582 at C_{Bi} =0.5 while the experimental value of S_M/R is 0.7051 at C_{Bi} =0.5.

C. Heat of mixing (H_M)

The heat of mixing (H_M) for the alloy is calculated using equation (10) with the help of theoretical values of order energy parameter which is shown in figure 3.

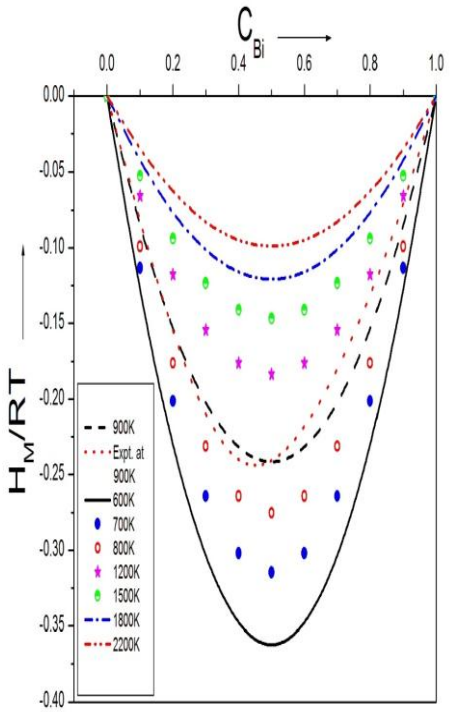

Figure 3. Graph for H_M/RT versus the concentration of C_{Bi} of Bi-In liquid alloy at temperatures 900k, 600K, 700K, 800K, 1200K, 1500K, 1800K and 2200K.

At 900k, it was found that the theoretical and experimental values of H_M/RT are in agreement. The values of H_M/RT are negative in the entire concentration range i.e. C_{Bi}=0.1 to 0.9. The minimum value of H_M/RT (i.e. H_M/RT= -0.24475 at C_{Bi}=0.5).

At temperatures 900k, 600K, 700K, 800K, 1200K, 1500K, 1800K and 2200K the minimum value is at C_{Bi} = 0.5. Thus, the symmetry in heat of mixing is well explained. As the temperature of the alloy is increased from 600k to 2200K, the values of H_M/RT increases.

D. Activity

Activity of Bi and In atoms of the alloy is Calculted using equations (5) and (6) in entire concentration range. The activity (Ln a) versus the concentration is studied which is shown in figure 4 and figure 5.

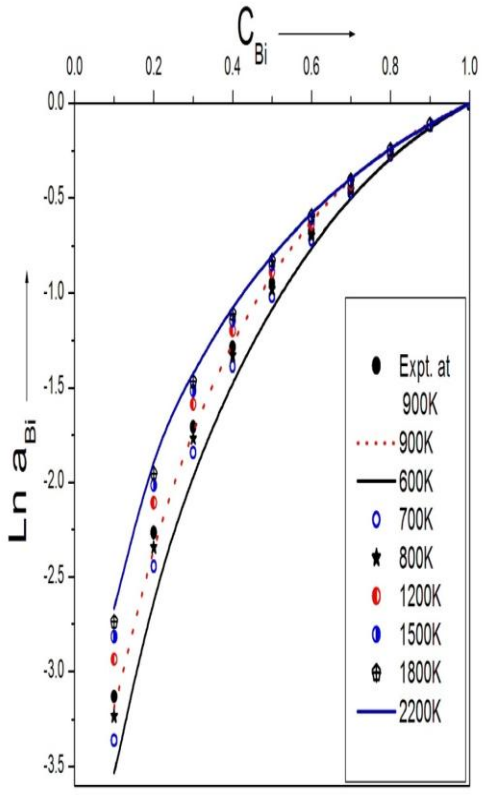

Figure 4. Ln a_{Bi} versus C_{Bi} of Bi-In liquid alloy at 900k, 600K, 700K, 800K, 1200K, 1500K, 1800K and 2200K.

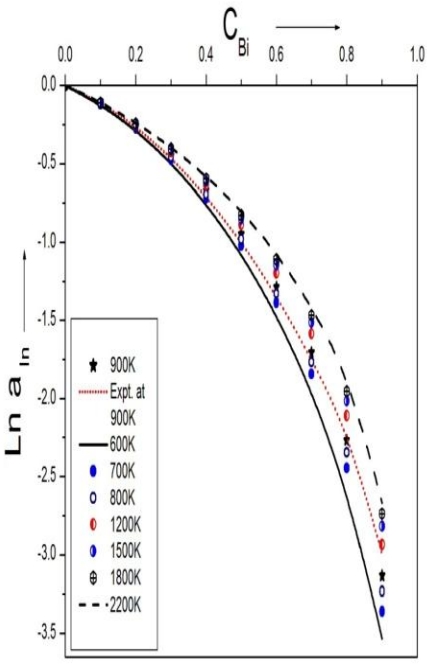

Figure 5. Ln a_{In} versus C_{Bi} of Bi-In liquid alloy at 900K, 600K, 700K, 800K, 1200K, 1500K, 1800K and 2200K.

The values of activity (Ln a) of both the components i.e. Bi and In of the alloy are in good agreement with the experimental values for whole range of concentration at 900K. The value of activity (Ln a) is minimum at 600k and maximum at 2200K i.e. when the temperature is increased from 600k to 2200K, the values of activity (Ln a) increases.

E. Transport properties: chemical diffusion and viscosity

Equation (13) is used to calculate the diffusion coefficient (D_M/D_{id}) with the help of theoretical values of order energy parameters ω(T). The investigation of the diffusion coefficient with the concentration of Bi is shown in figure (6).

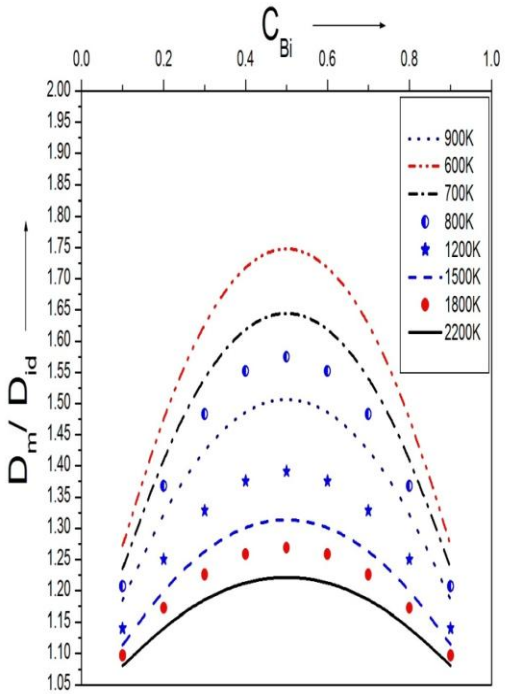

Figure 6. Ratio of mutual and self-diffusivities, D_M/D_{id} for Bi-In liquid alloy at temperatures 900k, 600K, 700K, 800K, 1200K, 1500K, 1800K and 2200K versus concentration of Bi.

The value of $\frac{D_M}{D_{id}} > 1$ in the entire range of concentration at temperatures 600K, 700K, 800K, 900k, 1200K, 1500K, 1800K and 2200K which shows chemical order in the alloy. The ordering tendency of the atoms in Bi-In liquid alloys is greater about equiatomic composition as the maximum value of D_M/D_{id} is at C_{Bi} = 0.5. The value of diffusion coefficient is minimum at 600K and maximum at 2200K. As the temperature increases from 600k to 2200K, the values of diffusion coefficient increases at the whole concentration range i.e. C_{Bi} = 0.1 to 0.9.

Viscosity of the alloy is calculated using equations (14) and (15). The viscosities of pure components Bi and In at temperatures 900k, 600K, 700K, 800K, 1200K, 1500K, 1800K and 2200K is computed using equation (15) which is used to find the viscosity of the alloy for corresponding temperatures using equation (14) . The viscosity of pure component can be obtained with the help of constants η_{ok} and E for the metals [20].

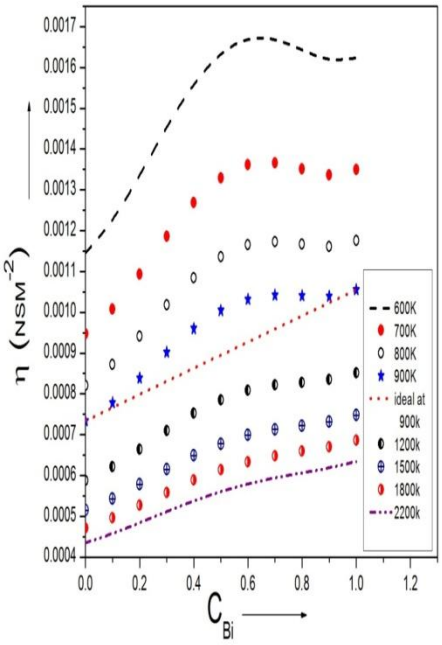

Figure 7. Viscosity of Bi-In liquid alloy at 900k, 600K, 700K, 800K, 1200K, 1500K, 1800K and 2200K versus concentration of Bi.

The viscosity of the alloy is slightly deviated from ideal values at the concentration C_{Bi}=0.1 to 0.9 at 900K. The viscosity of pure component of Bi atom is more than the viscosity of pure component In at temperatures 600K, 700K, 800K, 900k, 1200K, 1500K, 1800K and 2200K. The viscosity of the alloy increases with the increase in temperature from 600k to 2200K at each concentration range and maximum at 2200K. As the concentration of Bi atom increases, the viscosity of the alloy increases at all temperatures of study.

F. Structural properties

The values of Short range order parameter (α_1) at temperatures 600K, 700K, 800K, 900K, 1200K, 1500K, 1800K and 2200K are calculated from equation (19) with the help of values of concentration fluctuation in the long wavelength limit ($S_{cc}(0)$) at corresponding temperatures. The theoretical and experimental values of concentration fluctuation in the long wavelength limit ($S_{cc}(0)$) can be obtained from equations (18) and (19).

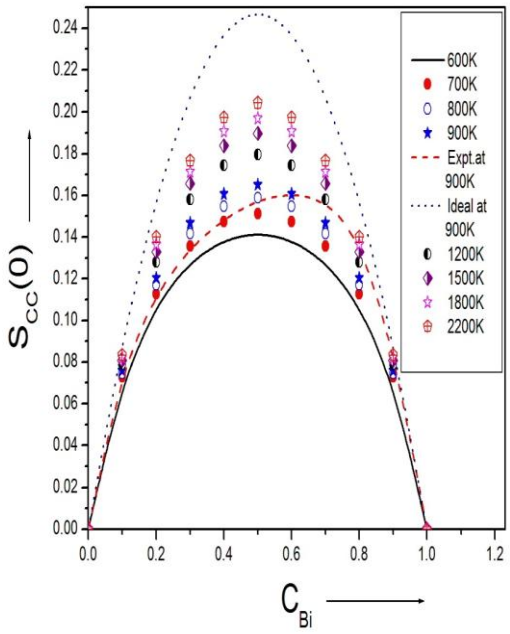

Figure 8. Theoretical values of Concentration fluctuation of Bi-In liquid alloy at 900k, 600K, 700K, 800K, 1200K, 1500K, 1800K and 2200K along with experimental values at 900K and $S_{cc}^{id}(0)$.

The calculated values of $S_{cc}(0)$ are in well agreement with the experimental values [5] and the values of $S_{cc}(0)$ are less than the ideal values at all the concentrations at 900K. Also, the theoretical value of $S_{cc}(0)$ is maximum at C_{Bi} =0.5 i.e. 0.1651 and experimental value is maximum at C_{Bi} =0.6 i.e. 0.1610.

The maximum value is at C_{Bi} =0.5 at temperatures 600K, 700K, 800K, 1200K, 1500K, 1800K and 2200K which indicates the symmetry in $S_{cc}(0)$ for Bi-In liquid alloy. As the temperature of study increases, the values of $S_{cc}(0)$ increases at each concentrations i.e. the maximum value of $S_{cc}(0)$ is at 2200K. Also, It is obtained that $S_{cc}(0) < S_{cc}^{id}(0)$ throughout the entire concentration range at all temperatures of investigation which indicates that hetero-coordination is favored in the Bi-In alloy.

The Warren-Cowley chemical short-range order parameter (α_1) [19], [24] is Calculated from equation (19) using the theoretical values of $S_{cc}(0)$. We have calculated that the Chemical short range order parameter (α_1) is negative at all the concentrations which are in support of ordering nature of the alloy.

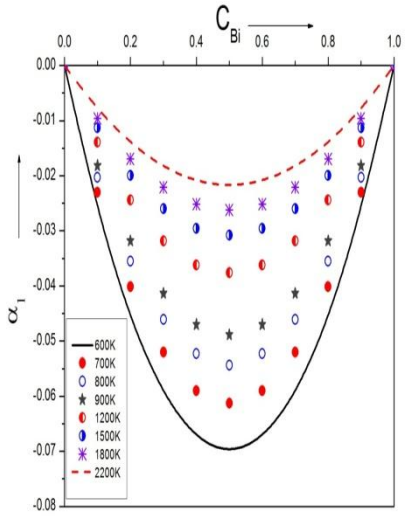

Figure 9. Chemical short range order parameter (α_1) of Bi-In liquid alloy at 900k, 600K, 700K, 800K, 1200K, 1500K, 1800K and 2200K with co-ordination number (Z)= 10.

The Chemical short range order parameter (α_1) at temperatures 600K, 700K, 800K, 900k, 1200K, 1500K, 1800K and 2200K is minimum at C_{Bi}= 0.5 which indicates symmetry. The value of α_1 increases as the temperature increases from 600k to 2200K in each concentration range.

IV. CONCLUSION

-The Bi-In liquid alloy is an ordered system and weakly interacting in nature.
-The interchange energy is negative and temperature dependent.
-The value of free energy of mixing and heat of mixing increases as the temperature increases in all temperatures of investigations and symmetry is observed in both.
-The activity of the alloy slightly increases as the temperature of study increases at each concentration range.
-The diffusion coefficient decreases as the temperature increases.
-Viscosity is temperature dependent and decreases as the temperature of study increases.

- The symmetry in Concentration fluctuation and Chemical short range order parameter is observed, and increases its value as the temperature of study increases.

REFERENCES

[1] K. Suganuma,Lead-Free Soldering in Electronics, CRC Press, 1st edition, December 2003.

[2] R. Novakovic, D. Giuranno, E. Ricci, T. Lanata, S. Amore "Experimental and Computational investigation of intermetallic systems: A Special Issue Dedicated to Prof. Riccardo Ferro," Calphad, Issue 1, Volume 33, 69, 2009.

[3] D.R. Frear, J.W. Jang, J.K. Lin, C. Zhang, JOM (Applied Material Science and Engineering), Vol.53, Issue 6, 28-33,2001.

[4] I. Kirschner, J. Bankuti, G. Kiss, I. Kovacs, L. Laszloffy, G. Remenyi And K. Sajo , "Magnetic properties of Superconducting In-Bi alloys," Soviet Physics- Journal of Experimental and theoretical physics, , Vol.3,No.39,1054-1058, 1974.

[5] R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser and K. K. Kelley, " selected Values of the Thermodynamic Properties of Binary Alloys," Metal Park, ASM International, Ohio, 1973.

[6] Okamoto, H., Massalski, T.B. Phase Diagrams of Indium Alloys and Their Engineering Applications, in: C.E.T. White, H. Okamoto (Eds.), Monograph Series on Alloy Phase Diagrams, ASM International, Materials Park, Ohio, pp. 46-54, 1992.

[7] V.T. Witusiewicz, U. Hecht, B. Bottger, S. Rex, J. "Thermodynamic Re-Optimization of the Bi-In-Sn System based on New Experimental Data," Journal of alloys and compounds, 428(1), pp. 115-124, Jan. 2007.

[8] K. K. Mishra, H. K. Limbu, B. Yadav, A.K. Khan, I.S. Jha, D. Adhikari, "Thermodynamic, structural, surface and transport properties of Zn-Cd liquid alloy at 800K," Bibechana, 54- 65,2017.

[9] R. N. Singh and F. Sommer, "Segregation and immiscibility in liquid binary alloys," Reports Prog. Phys., vol. 60, no. 1, pp. 57– 150, Jan. 1997.

[10] T. Tanaka, K. Hack, T. Iida and Hara, "Application of thermodynamic databases to the evaluation of surface tensions of molten alloys, salt mixtures and oxide mixtures," Zeitschrift Fuer Met., vol. 87, pp. 380–389, 1996.

[11] P.J. Flory, "Thermodynamics of High Polymer Solutions," J. Chem. Phys. **10 (**1942) 51.P.J. Flory, J. Chem. Phys. **10 (**1942) 51.

[12] E.A. Guggenheim, "Mixture" Oxford University Press, Oxford. (1952).

[13] E. A. Moelwyn - Hughes, "Physical Chemistry," Oxford, London : Longmans Green and Co., 1974.

[14] H. K. Limbu, K. K. Mishra, J. Nirala, I.S. Jha, B.P. Singh, D. Adhikari, "Thermodynamic, microscopic and surface Properties of Zn-In liquid alloy at 700K," IOSR Journal of applied Physics (IOSR-JAP), 2278- 4861.Volume 9, Issue 1 Ver. I , PP. 58-66. (Jan. – Feb.), 2017.

[15] A. B. Bhatia, W. H. Hargrove, and N. H. March, "Concentration fluctuations in conformal solutions and partial structure factor in alloys," J. Phys. C Solid State Phys., vol. 6, no. 4, pp. 621–630,Feb.1973.

[16] A. B. Bhatia and V. K. Ratti, "Number concerntration strucure factors and their long wave-length limit in multicomponent fluid mixture," Phys. Chem. Liq., vol. 6, pp. 201–213, 1977.

[17] B. P. Alblas, C. van der Marel, W. Geertsma, J. A. Meijer, A. B. van Oosten, J. Dijkstra, P.C. Stein, and W. van der Lugt, "Experimental results for liquid alkali-group IV alloys," J. Non. Cryst. Solids, vol. 61–62, pp. 201–206, Jan. 1984.

[18] R. N. Singh and F. Sommer, Thermodynamic investigation of Viscosity and diffusion in binary liquid alloys. Phys. Chem. Liq. Vol. 36 , pp. 17-28, 1998 .

[19] J. M. Cowley, "An Approximate Theory of Order in Alloys," Phys. Rev., vol. 77, no. 5, pp. 669–675, Mar. 1950.

[20] E. A. Brandes and G.B. Brook, Ed., Smithells Metals Reference Book, 7th edition, Butterworth-Heinemann Linacre House, Jordan Hill, Oxford, 1992.

[21] R.N. Singh and A.B. Bhatia, "Flory's formula for the entropy of mixing of NaCs alloy," J. Phys. F:Met.Phys. Vol. 14, 2309-2314, 1984.

[22] F. E. Neale and N. E. Cusack, "Thermodynamic properties of liquid sodium-caesium alloys" J. Phys. F: Met. Phys. 12, 2839, 1982.

[23] A. B. Bhatia and R. N. Singh, "Thermodynamic Properties of Compound Forming Molten Alloys in a Weak Interaction Approximation," Phys. Chem. Liq., vol. 11, no. 4, pp. 343– 351, May 1982.

[24] B. E. Warren, X-ray diffraction, Addison-Wesley, Reading MA, 1969