4.1 Introduction

Conventional Pb-Sn solder is the most reliable solder alloys in electronic interconnection industries. It may be because of its very attractive properties like low melting point, manufacturability and reliability. No such soldering alloys have been found till date to replace the Pb-Sn solder. The problem with the current soldering alloys is the toxicity of lead. It has many harmful effects on health and the environment. Therefore, the use of Pb-Sn solders is going to be ceased very soon. Many electronic industries are thinking of switching to any alternative materials that is free of lead. Now researchers are working hard to develop the lead-free solder alloys. It has been seen that it is not at all easy to replace lead by any single metal. People are trying to develop higher order alloys that are lead-free. One such type of alloy is Bi-In-Zn-Sn. It is a quaternary system having many ternary and many binary systems. To measure the thermodynamic properties of the quaternary system is very difficult. Therefore, researchers are trying for the estimation of thermodynamic properties from the measured data of lower order system like ternary and binary and suitable theoretical model. Before we go for the measurement of thermodynamic properties of ternary system, it is essential to determine the thermodynamic properties of the binary systems as we need binary data for the computation of ternary properties. Activity measurements of the binary systems are available in the literature. But, very few reliable calorimetric data are available in the literature. Accurate binary date is very important as the ternary data depends on the binary data and quaternary data depends on the ternary data and so on. Actually, the starting point is the binary systems and its measured thermodynamic data. Once we have accurate thermodynamic data of binary systems, our prediction or estimation of thermodynamic properties for the higher order system will have better accuracy. Therefore, this chapter dealt with calorimetric measurements of binary system using MHTC 96 line evo calorimeter.

4.2 Literature Review

4.2.1 Bi-Sn System

The alloy Bi $_{42}$Sn $_{58}$ could substitute the conventional Pb solder due to low melting point of 412 K. is a potentially attractive substitute for toxic lead solders since it has a low melting point of 412 K. The soldering properties as like mechanical properties are studied for the Bi-Sn based multicomponent alloys. Some of such alloys having high melting point are reported in the literature [Cormack et al. (1997), Rejent (1999), Sabbah et al. (1999), Suganuma and Opin (2001), Vianco and Xia and Shi (2002)] have measured the enthalpy of mixing for Bi-Sn system.

The enthalpy of mixing of liquid Bi-Sn alloys was measured by Samson-Himmelstjerna [Samson-Himmelstjerna (1936)]. Interaction parameters have been computed based on EMF measurements by Asryan and Mikula [Asryan and Mikula (2004)] at 450^{o}C. These data are in very good agreement with earlier calorimetric measurements by Wittig and Huber [Wittig and Huber (1958)] at 470^{o}C by Yazawa et al. [Yazawa et al.(1968)] at 417^{o}C, and by Sharkey and Pool [Sharkey and Pool (1972)] at 452^{o}C as well as with EMF data reported by Seltz and Dunkerley [Seltz and Dunkerley (1942)] for 335^{o}C. The enthalpy of mixing was found to be independent of temperature for Bi-Sn system within the experimental errors. The key to predicting the properties of multicomponent systems lies in knowing their thermodynamic characteristics and phase diagrams, which, in turn, requires information about the constituent binary systems, in particular, in the liquid state [Lee and Lee (2001), Lutsyk and Vorobeva (2015), Ohtani and Ishida (1994), Kattner and Boettinger (1994), Shevchenko et al. (2016)]. Bi and Sn form a eutectic at 57 at % Sn with a melting point of 412 K [Massalski (1986)].

The thermodynamic functions of mixing recommended in [Predel and Bornstein (1992)] for the Bi–Sn system were obtained before 1965. The data obtained for this system in different studies cited in scatter widely and are in many respects inconsistent. Later many authors has measured and compared at same system. The mixing enthalpies of solution they obtained are in reasonable agreement with the data given in [Hultgren et al. (1973)]. In contrast to what was reported previously, Cho et al. [Cho et al. (1990)] obtained an exothermic enthalpy of mixing for Bi–Sn melts. All of the thermodynamic functions of mixing reported in Cho et al. [Cho et al. (1990) and Cho et al. (1997)] vary randomly with composition. This behavior was attributed to a particular character of the Bi–Sn system. The purpose of this work was to determine the thermodynamic functions of mixing in the Bi-Sn system using emf measurements. The considerable amount of thermodynamic data is available on the enthalpy for liquid Bi-Sn alloys. So the calorimetric investigations on Bi-Sn binary system were taken up in the present study. A fully automated solution calorimeter has been used to measure the enthalpy of mixing by dropping indium on bismuth at the 767,813 and 855 K over the entire range of compositions.

4.2.2 Bi-In system

The objective of thermodynamic investigations is the evaluation of the partial and integral thermodynamic quantities and their dependency on concentration, pressure and temperature. Various thermodynamic techniques are available, depending on the system and the required properties to be measured. The higher order systems may be calculated based on the binary and ternary data. Various extrapolation and theoretical models are available and are very extensively used.

The enthalpy of mixing of liquid Bi-In alloys were measured by Gregorczyk et al. [Gregorczyk et al. (1981)] using an electromotiveforce (EMF) method and calorimetric method by Wittig and Muller [Wittig and Muller (1959)]. The thermodynamic data of liquid alloys were compiled by Hultgren et al. [Hultgren et al. (1963)] at 627^{o}C. The thermodynamic properties of the liquid phase of Bi-In were evaluated by Chevalier et al. [Chevalier (1988)] using the CALPHAD method.

Although a series of alloys for the replacement of lead bearing solders is already in use, Bi- In-Zn is still a multi component system that might also be suitable as a lead-free solder. One system that has been chosen as a lead-free solder material is the eutectic mixture of binary Sn-Zn, which has a suitable melting point of 470 K (197^{o}C). The disadvantages of the solder are that zinc is very prone to oxidation and that the solder shows poor wettability compared to eutectic Sn-Pb solder. The wettability can be enhanced by adding elements such as Bi and In to the binary alloy. Thermodynamic properties of Bi-In can be calculated from phase diagrams. The above author has explained that the enthalpies of formation and fusion can be measured by calorimetric or EMF. But the value of the enthalpies estimated from calorimetric data is correct mostly due to availability of reliable heat capacities data in the required temperature range. So, electrochemical techniques use for free energy. The combine enthalpy and free energy arrive at reliable values of entropies.

4.2.3 In-Sn system

In recent days, researchers are giving more attention on lead free solder materials specially In–Sn based alloys due to their good alloying tendency with copper etc [Gnecco et al. (2007), Moelans et al. (2003), and Morris et al. (1993)] for soldering the copper wire specially in electronic equipments. The enthalpy of mixing of liquid In-Sn system first has been measured by Kleppa [Kleppa (1956)] at 450^{o}C from 6 to 34 at. % In by means of direct-reaction calorimetry. It was followed by Wittig and Scheidt [Wittig and Scheidt (1961)] using same instrument for the entire composition range at

371^{o}C. The same method was used by Yazawa et al. [Yazawa et al. (1968)] at 450^{o}C from 19 to 90 at. % In and finally by Bros and Laffitte [Bros and Laffitte (1970)] at 248^{o}C over the entire composition range. Prior to 1971 Values for the integral enthalpy published were collected by Hultgren et al. [Hultgren et al. (1973)], and the agreement among these authors is generally quite good. These experimental data show small negative values for the enthalpy of mixing of liquid In–Sn alloys. Several thermodynamic assessments of the In–Sn system were presented by Lee et al. [Lee et al. (1996)], by Korhonen and Kivilahti [Korhonen and Kivilahti (1998)], and more recently by David et al. [David et al. (2004) based on these experimental data. In all these cases good agreement was obtained between calculated and experimental data. The most recent experimental investigation of the enthalpy of mixing, using direct-reaction calorimetry at 900 ◦C over the entire composition range, was by Luef et al. [Luef et al. (2004)]. Several lead free systems have been investigated by different author [Janke et al. (2010), Zivkovic et al., (2007).and Zivkovic et al. (2010)].

The enthalpy of formation and the activities of this liquid system have been determined by Hultgren et al. and Vassiliev et al. [Hultgren et al (1973) and Vassiliev et al. (1998)] at temperature 520-820 K. The re-assessment of the In-Sn phase diagram [David et al. (2004)] was done by these experimental data. It is due to negative deviation from the ideal mixing and, slightly improved with respect to its previous versions [Massalski (1986), Lee et al. (1996)]. The earlier phase diagram [David et al. (2004)] of In-Sn system which was accepted is mainly based on the work by Heumann and Alpaut [Heumann and Alpaut (1964)]. The main discrepancy between the phase diagram [Hansen and Anderko (1958)] and the later accepted one [Massalski (1986)] is the stability region of two intermediate phases, the Sn-rich γ-phase and In-rich β- phase.

But still a considerable uncertainty regarding the phase equilibria between γ and bct (Sn) phases. In this two phase region γ + bct (Sn) lies between about 88-93 at% Sn at room temperature reported by Heumann and Alpaut [Heumann and Alpaut (1964)]. While Predel and Gsdecke [Predel and Sdecke (1975)] reported it lies between 86-97 at% Sn. later Koyama et al [Koyama et al. (1984)] reported that Sn-(8.0-9.5) at% In alloys undergo a martensitic transformation between the γ and bct (Sn) structures with varying temperature. The solubility of In in Sn in the temperature range 80 to 130^{o}C using the measurements of resistances and γ single phase region has been observed by Wojtaszek and Kuzyk [Wojtaszek and Kuzyk (1974)]. According to this, γ +bct (Sn) two phase region lies between 90-94 at% Sn at 120^{o}C and between 89-92.5 at% Sn at 80^{o}C. The statistical thermodynamic approach of Bhatia and Thornton [Bhatia (1970)] shows the lacking these experimental data. This experimental will be approachable for accurate determination of phase diagram.

4.3 Experimental Procedure

4.3.1 Materials

High purity metals (Bi, Sn and In) were used in the present investigations. α-Al_2O_3 needles obtained from Johnson Matthey, U. K were used as calibration standard. Fine sandpaper was used to remove the oxide layer on the surface of Indium ingot. All the pure metals and chemicals were used as supplied and listed in Table 4.1.

Table 4.1 Purities and sources of materials used in the present study

Raw materials	Source	Initial purity (wt. %)
Bismuth (Lumps)	Johnson Matthey, U. K	99.999
Tin (Shots)	Johnson Matthey, U. K	99.999
Indium (Ingots)	Johnson Matthey, U. K	99.999
Argon gas	Indian oxygen limited, India	>99

4.3.2 Drop calorimetric measurements

MHTC96 high temperature drop calorimeter made from Seta ram, France was used for these measurements. It is a calorimeter with a thermopile of 20 thermocouples and a graphite tube resistance furnace operating up to 1723K. A motorized dropping device (Multisample Introducer) is placed on the top of the calorimeter. Maximum of 23 numbers of samples can be charged at a time into the multi sample introducer and the timer has been set to drop the sample automatically at a regular interval of time. The inlet water pressure of the calorimeter was also checked before the start of the experiment. Then, required quantity of bismuth (n_{Bi} = 0.002153 mole) was charged in an alumina crucible and furnace was heated to the desired temperature as per the programme. Dropping of the sample started 1 hour after attaining the required temperature. Measured quantity of Tin, Indium and Indium has dropped for Bi-Sn, Bi-In and In-Sn respectively by a motorized dropping device in a fixed interval of 30 minutes to prevent oxidation of the samples all measurements were taken in an atmosphere of flowing argon. At the end, four numbers of α-Al_2O_3 needles were dropped for the calibration of the equipment. Control and data evaluation were performed using the CALISTO software provided by the manufacturer. Reproducibility of the data was checked by repeating the experiments at the above temperatures once more.

4.4 Results and Discussion

4.4.1 Enthalpy of mixing

The measured enthalpy of mixing is given by

$$\Delta H_{In,i}^{Reaction} = \left(\Delta H_{In,i}^{Signal} . K\right) - \left(\Delta H_{In,i}^{T_D \to T_M} \; . \; n_{In,i}\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.1)$$

Where$n_{In,i}$ is the number of moles of the indium added at i - th drop. $\Delta H_{In,i}^{Signal}$is the heat effect due to single i-th drop of indium sample to the bath; K is the calorimeter constant;$\Delta H_{In,i}^{T_{D}\rightarrow T_{M}}$ is the enthalpy change of 1 mole of indium from drop temperature T_D (in Kelvins) to the bath temperature T_M, in the i-th measurement. The molar enthalpy difference$\Delta H_{In,i}^{T_{D}\rightarrow T_{M}}$for indium was calculated using the polynomial of pure elements from Dinsadale[Dinsadale (1991)].

Because of the relatively small mass added the Partial enthalpy can be directly calculated as:

$$\Delta \overline{H_{\iota}} = \frac{\Delta H_{Reaction}}{n_{i}} \qquad \text{……………………………………………………………………………………… (4.2)}$$

The integral enthalpy of mixing was calculated by summarizing the respective reaction enthalpies and division by the total molar amount of the binary alloys.

$$\Delta_{mix} H = \frac{\Sigma \Delta H_{Reaction}}{(n_{Crucible} + \Sigma n_{i})}) \qquad \text{……………………………………………………………………………… (4.3)}$$

The molar enthalpy difference$\left(H_{Sample,T_C} - H_{Sample,T_D}\right)$ for Indium was calculated using the following relation.$\left(H_{Sample,T_C} - H_{Sample,T_D}\right) = \int_{T_D}^{T_C} C_P dT$

$$\left(H_{Sample,T_C} - H_{Sample,T_D}\right) = \int_{T_D}^{T_{Tr}} C_P dT + \Delta H_{T_{Tr}} + \int_{T_{Tr}}^{T_m} C_P dT + \Delta H_{T_f} + \int_{T_m}^{T_c} C_P dT \text{.... ……………………………………………………………………(4.4)}$$

Where T_D = Dropping (Room) Temperature,T_{Tr} = Transformation Temperature, $\Delta H_{T_{Tr}}$ = Enthalpy change during transformation*,T_m = Melting Point, ΔH_{T_f}= Enthalpy change during melting, T_C = Temperature of the Calorimeter at which experiment is carried out. and Cp = heat capacity [Kubaschewski et al. (1967)]. Integral molar enthalpies of mixing of the Bi-Sn binary system obtained from experiments are presented in Table 2 (pure liquid component is the reference state).

Table 4.2 Integral enthalpy of mixing resulting from calorimetric measurements of Bi-Sn System with Tin dropped at 767, 813 and 855 K. Standard states: pure liquid metals

No. of moles of tin (n_{Sn}) [mole]	**Mole fraction x_{Sn}**	**Standard uncertainties u (x_{Sn})**	**Heat effect $\Delta H_{Signal} . K$ (J)**	**Standard uncertainties $\Delta H_{Signal} . K$ (J)**	**Heat of reaction $\Delta H_{Reaction}$ (J)**	**Integral enthalpy $\Delta mixH$ (Jmole-^{1})**
Series 1: Bi-Sn alloys; Atmosphere: Argon at pressure p = 0.1 MPa, starting amount n_{Bi} = 0.002153 mole, K = 0.0036571 JμVs^{-1}, T_D = 298 K, T_M = 767 K						
0.000232	0.0973	0.0001	4.836	0.007	0.061	25.58
0.000310	0.2011	0.0001	6.468	0.025	0.088	55.29
0.000418	0.3084	0.0001	8.721	0.016	0.118	85.77
0.000530	0.4090	0.0002	11.04	0.018	0.130	109.0
0.000689	0.5030	0.0002	14.32	0.067	0.140	124.0
0.001102	0.6038	0.0001	22.85	0.066	0.170	130.1
0.001691	0.6978	0.0001	34.94	0.154	0.140	118.88
0.003561	0.7985	0.0002	73.4	0.133	0.110	89.56
0.005028	0.8630	0.0002	103.53	0.181	0.030	62.81
Series 2 : Bi-Sn alloys; Atmosphere: Argon at pressure p = 0.1 MPa, starting amount n_{Bi} = 0.002153 mole, K = 0.0037225 JμVs^{-1}, T_D = 298 K, T_M = 813 K						
0.000245	0.1022	0.0001	5.416	0.022	0.064	26.69
0.000314	0.2061	0.0001	6.953	0.030	0.094	58.26
0.000364	0.3001	0.0002	8.06	0.016	0.109	86.80
0.000537	0.4041	0.0002	11.87	0.024	0.140	112.6
0.000705	0.5014	0.0001	15.55	0.081	0.150	129.0
0.001138	0.6054	0.0001	25.03	0.099	0.170	133.2
0.001704	0.6993	0.0002	37.38	0.169	0.160	123.88
0.003785	0.8033	0.0002	82.8	0.153	0.120	92.01
0.004853	0.8637	0.0001	106.03	0.178	0.030	65.64
Series 3: Bi-Sn alloys; Atmosphere: Argon at pressure p = 0.1 MPa, starting amount n_{Bi} = 0.002153 mole, K = 0.00380285 JμVs^{-1}, T_D = 298 K, T_M = 855 K,						
0.000220	0.0927	0.0001	5.122	0.011	0.067	28.23
0.000274	0.1866	0.0001	6.38	0.038	0.081	55.91
0.000388	0.2906	0.0001	9.029	0.024	0.114	86.3
0.000463	0.3845	0.0001	10.760	0.027	0.120	109.2
0.001007	0.5221	0.0002	23.35	0.103	0.210	131.4
0.000958	0.6059	0.0002	22.16	0.042	0.150	135.8
0.001403	0.6864	0.0002	32.37	0.141	0.130	127.0
0.002238	0.7635	0.0002	51.55	0.230	0.130	110.06
0.002258	0.8105	0.0001	51.93	0.098	0.050	92.59

0.004275	0.8623	0.0002	98.25	0.1571	0.030	69.19

[a] Standard uncertainties u are: u(T_D)=1 K, u(T_M)=1 K, u(p)=10 kPa, u(n_{Bi})=0.000001 mole, u(n_{Sn})=0.000002 mole, u($H_{Diss\text{-}x}$) =0.001 kj; Series 1: u(K)=0.00001 J µV s^{-1}, u(Δ_{mix}H) = 0.0253 kJ mol^{-1}; Series 2: u(K)=0.00002 J µV s−1, u(Δ_{mix}H)=0.0294 kJ mol–^{1}; Series 3: u(K)=0.00001 J µV s^{-1}, u(Δ_{mix}H) = 0.0332 kJ mol^{-1}

Table 4.3 Integral enthalpy of mixing resulting from calorimetric measurements of Bi-In System with indium dropped at 767, 813 and 855 K. Standard states: pure liquid metals

No. of moles of Indum (n_{In} mole),	**Mole fraction x_{In}**	**Standard uncertainties u (x_{In})**	**Heat effect $\Delta H_{Signal}.K$ (J)**	**Standard uncertainties $\Delta H_{Signal}.K$ (J)**	**Drop enthalpy $H_{Reaction}$(J)**	**Integral enthalpy $\Delta mixH$ (Jmol-^{1})**
Series 1: Bi-In alloys; Atmosphere: Argon at pressure p = 0.1 MPa, starting amount n_{Bi} = 0.003589 mole, k = 0.003533 J (µVs)$^{-1}$, T^D = 298 K, T^M = 767 K						
0.0003606	0.0913	0.0001	4.13	0.01	-1.96	-496
0.0005946	0.2102	0.0001	7.27	0.01	-2.77	-1042
0.0005734	0.2987	0.0002	7.27	0.01	-2.41	-1398
0.0009778	0.4112	0.0002	13.37	0.03	-3.15	-1691
0.0013988	0.5211	0.0002	21.56	0.05	-2.08	-1653
0.0022109	0.6302	0.0002	34.73	0.08	-2.64	-1549
0.0028042	0.7131	0.0001	46.25	0.11	-1.15	-1294
0.0053994	0.7996	0.0001	89.40	0.21	-1.87	-1008
0.0047485	0.8416	0.0001	79.84	0.19	-0.42	-816
0.0049709	0.8701	0.0001	83.51	0.20	-0.52	-688
0.0053277	0.8911	0.0001	90.19	0.21	0.12	-573
Series 2 : Bi-In alloys; Atmosphere: Argon at pressure p = 0.1 MPa, starting amount n_{Bi} = 0.003589 mole, k = 0.00359712 J (µVs)$^{-1}$, T^D = 298 K, T^M = 813 K						
0.0004125	0.1031	0.0002	5.56	0.01	-1.96	-492
0.0004640	0.1963	0.0002	6.26	0.01	-2.19	-933
0.0007404	0.3106	0.0002	10.49	0.03	-3.01	-1379
0.0007479	0.3972	0.0001	11.08	0.03	-2.55	-1636
0.0013171	0.5064	0.0001	21.91	0.06	-2.11	-1631
0.0016589	0.5981	0.0001	28.38	0.07	-1.89	-1540
0.0048842	0.7402	0.0001	87.04	0.24	-2.08	-1146
0.0055018	0.8142	0.0001	99.58	0.27	-0.82	-862
0.0056416	0.8562	0.0002	102.16	0.28	-0.78	-699

0.0044837	0.8781	0.0002	82.12	0.20	0.30	-582
0.0055041	0.8973	0.0001	100.35	0.28	-0.08	-493
Series 3: Bi-In alloys; Atmosphere: Argon at pressure p = 0.1 MPa, starting amount n_{Bi} = 0.003589 mole, k = 0.003703 J (μVs)$^{-1}$, T^D = 298 K, T^M = 855 K						
0.0003767	0.0981	0.0001	5.66	0.01	-1.67	-420
0.0005057	0.1998	0.0002	7.41	0.02	-2.43	-914
0.0006611	0.3026	0.0002	10.38	0.03	-2.48	-1280
0.0008483	0.4013	0.0001	13.67	0.04	-2.84	-1573
0.0013507	0.5114	0.0001	24.09	0.07	-2.20	-1584
0.0015867	0.5982	0.0002	29.28	0.09	-1.61	-1483
0.0031639	0.7033	0.0002	60.76	0.19	-0.84	-1165
0.0053003	0.7937	0.0001	102.02	0.32	-1.18	-878
0.0054045	0.8426	0.0001	105.69	0.33	0.45	-650
0.0052590	0.8721	0.0001	102.89	0.32	0.48	-511
0.0003767	0.0981	0.0001	5.66	0.01	-1.67	-420
0.0052938	0.8924	0.0001	103.72	0.33	0.63	-411

[a] Standard uncertainties u are: u(T_D)=1 K, u(T_M)=1 K, u(p)=10 kPa, u(n_{Bi})=0.000001 mole, u(n_{In})=0.000002 mole, u($H^{Reaction}$) =0.001 kj; Series 1: u(K)=0.00001 J μV s^{-1}, u(ΔH^m) = 0.0253 kJ mol^{-1}; Series 2: u(K)=0.00002 J μV s−1, u(ΔH^m)=0.0294 kJ mol–^{1}; Series 3: u(K)=0.00001 J μV s^{-1}, u(ΔH^m) = 0.0332 kJ mol^{-1}

Table 4.4 Integral enthalpy of mixing resulting from calorimetric measurements of In-Sn System with indium drop at 767, 813 and 855 K. Standard states: pure liquid metals

No. of moles of Indium (n_{In}) [mole],	**Mole fraction x_{In}**	**Standard uncertainties u (x_{In})**	**Heat effect $\Delta H_{Signal}.K$ [J]**	**Standard uncertainties $\Delta H_{Signal}.K$ [J]**	**Drop enthalpy $H_{Diss\text{-}x}$[J]**	**Integral enthalpy ΔH^m [Jmole-^{1}]**
Series 1: In-Sn alloys; Atmosphere: Argon at pressure p = 0.1 MPa, starting amount n_{Sn} = 0.003622 mole, k = 0.003401 J (μVs)$^{-1}$, T^D = 298 K, T^M = 767 K						
0.0004119	0.0004119	0.0004119	0.0004119	0.0004119	0.0004119	0.0004119
0.0004555	0.0004555	0.0004555	0.0004555	0.0004555	0.0004555	0.0004555
0.0007312	0.0007312	0.0007312	0.0007312	0.0007312	0.0007312	0.0007312
0.0008142	0.0008142	0.0008142	0.0008142	0.0008142	0.0008142	0.0008142
0.0012022	0.0012022	0.0012022	0.0012022	0.0012022	0.0012022	0.0012022
0.0020553	0.0020553	0.0020553	0.0020553	0.0020553	0.0020553	0.0020553
0.0025448	0.0025448	0.0025448	0.0025448	0.0025448	0.0025448	0.0025448
0.0053378	0.0053378	0.0053378	0.0053378	0.0053378	0.0053378	0.0053378
0.0041447	0.0041447	0.0041447	0.0041447	0.0041447	0.0041447	0.0041447

0.0047770	0.0047770	0.0047770	0.0047770	0.0047770	0.0047770	0.0047770
0.0060153	0.0060153	0.0060153	0.0060153	0.0060153	0.0060153	0.0060153
0.0031925	0.0031925	0.0031925	0.0031925	0.0031925	0.0031925	0.0031925
Series 2 : In-Sn alloys; Atmosphere: Argon at pressure p = 0.1 MPa, starting amount n_{Sn} = 0.003622 mole, k = 0.003460 J $(\mu Vs)^{-1}$, T^D = 298 K, T^M = 813 K						
0.0003807	0.0003807	0.0003807	0.0003807	0.0003807	0.0003807	0.0003807
0.0005311	0.0005311	0.0005311	0.0005311	0.0005311	0.0005311	0.0005311
0.0006391	0.0006391	0.0006391	0.0006391	0.0006391	0.0006391	0.0006391
0.0008851	0.0008851	0.0008851	0.0008851	0.0008851	0.0008851	0.0008851
0.0011330	0.0011330	0.0011330	0.0011330	0.0011330	0.0011330	0.0011330
0.0023661	0.0023661	0.0023661	0.0023661	0.0023661	0.0023661	0.0023661
0.0025007	0.0025007	0.0025007	0.0025007	0.0025007	0.0025007	0.0025007
0.0059541	0.0059541	0.0059541	0.0059541	0.0059541	0.0059541	0.0059541
0.0055549	0.0055549	0.0055549	0.0055549	0.0055549	0.0055549	0.0055549
0.0056919	0.0056919	0.0056919	0.0056919	0.0056919	0.0056919	0.0056919
0.0060802	0.0060802	0.0060802	0.0060802	0.0060802	0.0060802	0.0060802
Series 3: In-Sn alloys; Atmosphere: Argon at pressure p = 0.1 MPa, starting amount n_{Sn} = 0.003622 mole, k = 0.003584 J $(\mu Vs)^{-1}$, T^D = 298 K, T^M = 855 K						
0.0004259	0.0004259	0.0004259	0.0004259	0.0004259	0.0004259	0.0004259
0.0004786	0.0004786	0.0004786	0.0004786	0.0004786	0.0004786	0.0004786
0.0007436	0.0007436	0.0007436	0.0007436	0.0007436	0.0007436	0.0007436
0.0007951	0.0007951	0.0007951	0.0007951	0.0007951	0.0007951	0.0007951
0.0011980	0.0011980	0.0011980	0.0011980	0.0011980	0.0011980	0.0011980
0.0017584	0.0017584	0.0017584	0.0017584	0.0017584	0.0017584	0.0017584
0.0031334	0.0031334	0.0031334	0.0031334	0.0031334	0.0031334	0.0031334
0.0051928	0.0051928	0.0051928	0.0051928	0.0051928	0.0051928	0.0051928
0.0062191	0.0062191	0.0062191	0.0062191	0.0062191	0.0062191	0.0062191
0.0064683	0.0064683	0.0064683	0.0064683	0.0064683	0.0064683	0.0064683
0.0045282	0.0045282	0.0045282	0.0045282	0.0045282	0.0045282	0.0045282

[a] Standard uncertainties u are: u(T_D)=1 K, u(T_M)=1 K, u(p)=10 kPa, u(n_{Sn})=0.000001 mole, u(n_{In})=0.000002 mole, u($H_{Diss\text{-}x}$) =0.002 kj; Series 1: u(K)=0.00002 J $\mu V\ s^{-1}$, u(ΔH^m) = 0.00765 kJ mol^{-1}; Series 2: u(K)=0.00001 J μV s−1, u(ΔH^m)=0.00684 kJ mol–^{1}; Series 3: u(K)=0.00002 J $\mu V\ s^{-1}$, u(ΔH^m) = 0.0073 kJ mol^{-1}

[b] ^{TD}= Drop temperature in Kelvin, T_M= Bath temperature in Kelvin, n_{Sn}= no of moles of Tin, K= Drop calibration constant, ΔHSignal= It is the heat effect due to single drop of Tin sample to the bath.

The integral molar enthalpy of mixing is calculated at 767,813 and 855 K by equation (4.3) are shown in Table 4.2, 4.3 and 4.4. It contains information on the starting amounts, added amounts and the integral enthalpies of mixing of the liquid alloys. The enthalpy of mixing of Binary Bi-Sn system at 767, 813 and 855 K are calculated as discuss above are shown in Figure 4.1. $\Delta mixH$ *vs* x_{Sn} is plot taking composition of indium (xSn) as abscissa and the integral enthalpy of mixing as ordinate. It is endothermic so lead to immiscible but can be avoided at high temperature .The phase sepration for entire composition but it will be maximum at x_{Sn}~0.60. The interaction coefficient of Bismuth in Tin or Tin in Bismuth almost equal due symmetry on y axis (enthalpy of mixing) in Figure 4.1. It also reveals that as Sn composition increases the enthalpy of mixing increases but after x_{Sn}~0.60 it decreases as Sn composition increases. The maxima of the enthalpy curves are at x_{Sn}~ 0.60.

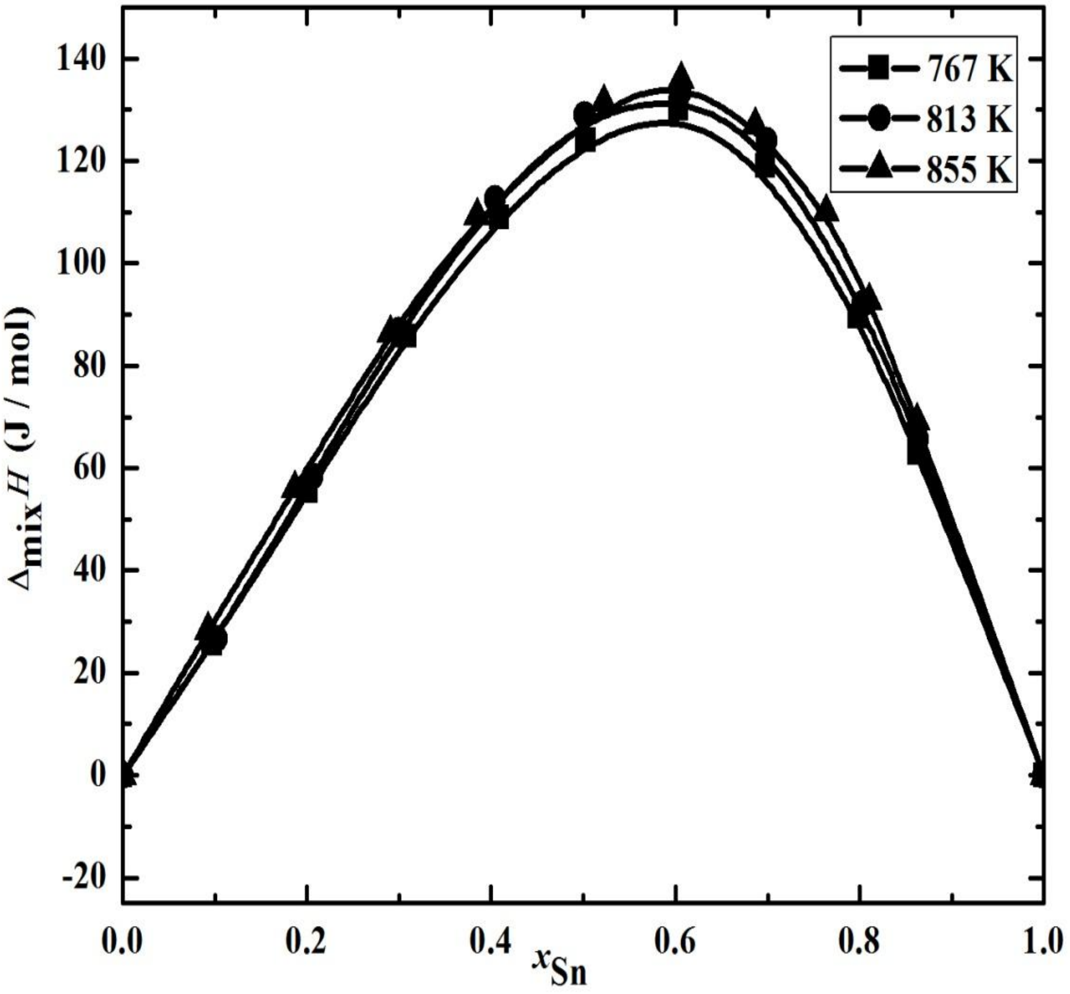

Figure 4.1 Integral molar mixing enthalpies of liquid Bi-Sn alloys at 767, 813 and 855 K.

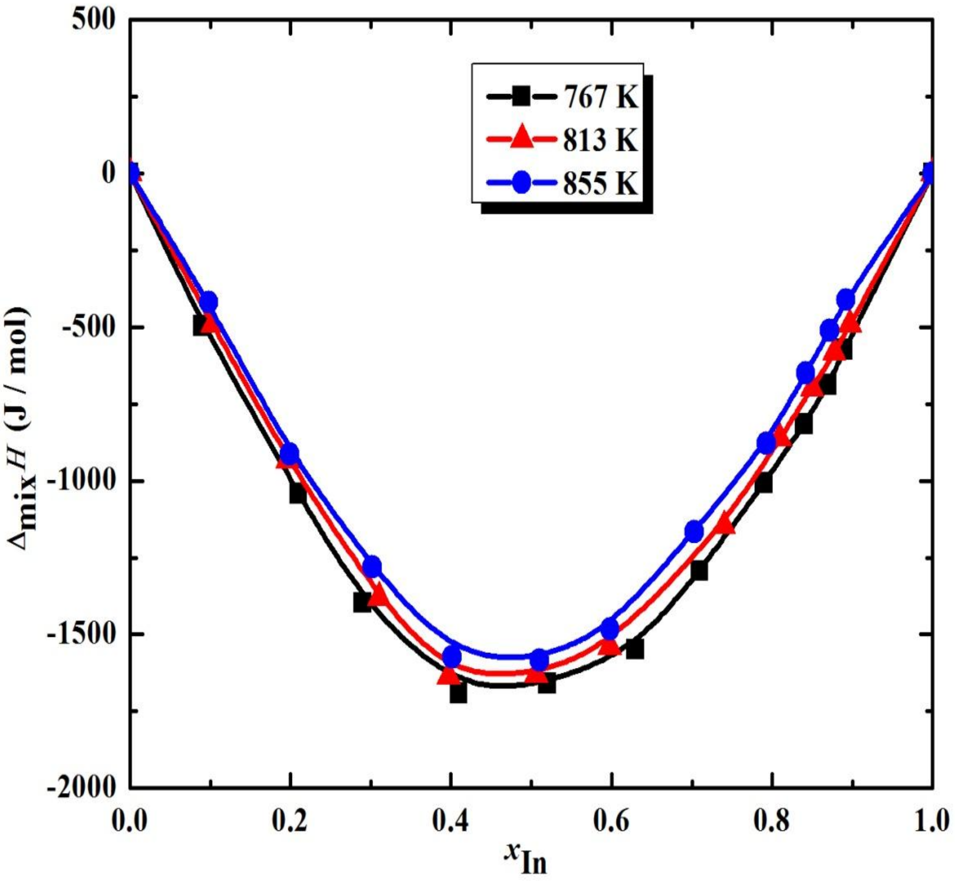

Figure 4.2 Integral molar mixing enthalpies of liquid Bi-In alloys at 767, 813 and 855 K.

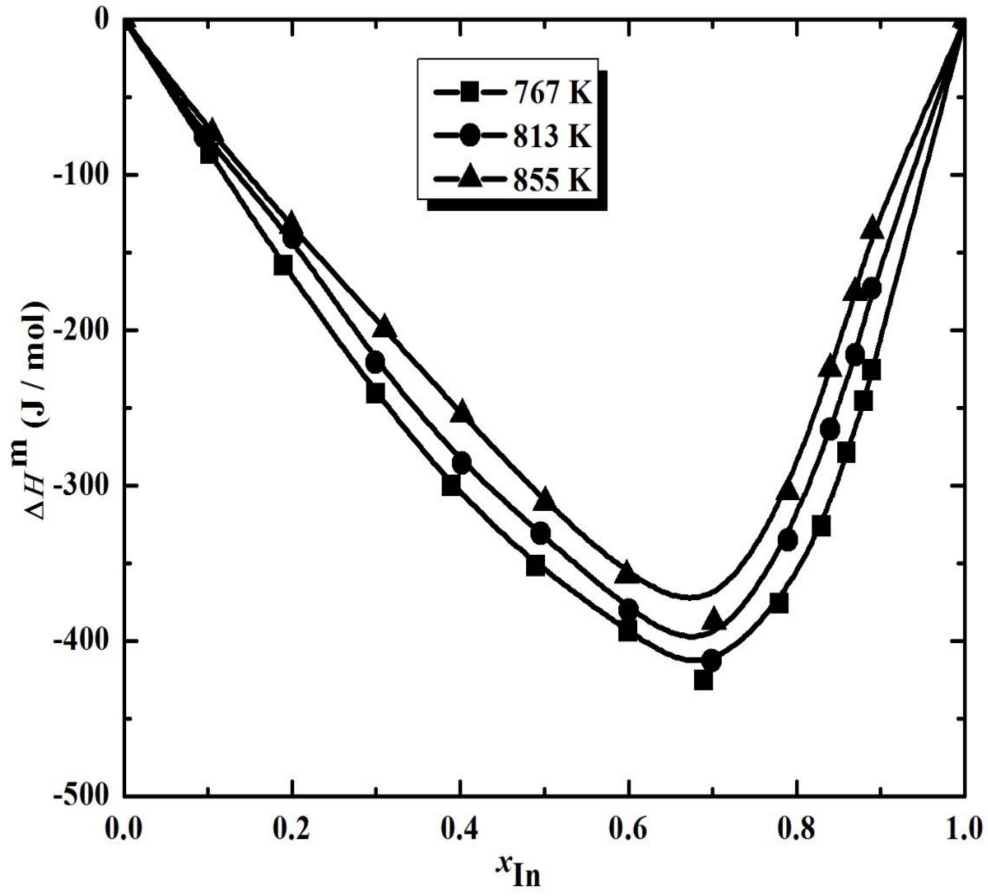

Figure 4.3 Integral molar mixing enthalpies of liquid In-Sn alloys at 767, 813 and 855 K.

It has also been observed that the integral enthalpy of mixing of this system is slightly dependent of with the variation of temperature for entire composition of Sn. As the temperature increases, the enthalpy of mixing becomes more endothermic.

The Bi-Sn shows endothermic while Bi-In and In-Sn system shows exothermic reaction. It is observed from the Figures 4.2 and 4.3 that enthalpies of mixing are continuous. So, the segregation or clustering of atoms in this system is ruled out. It can forms substitutional solid solution because of less atomic size difference as well as less electronegativity difference of Bi and In. As the temperature increases, the enthalpy of mixing becomes less exothermic. In general, a slightly temperature dependence of enthalpy of mixing is observed when the temperature is close to the liquidus and it becomes weak at higher temperatures. It can be explained according to the association theory for liquid alloys [Sommer (1982)] based on short range ordering in the liquid alloys at lower temperatures close to solidification. The minima in enthalpy of mixing curve represent the compositions of the ‘‘associates’’.

4.4.2 Theoretical modeling

The binary Bi–Sn, Bi-In and In-Sn system experimental calorimetric data for the enthalpies of mixing at 767,813 and 855 K were treated by a least squares fit using the following Redlich-Kister polynomial, as proposed by Ansara and Dupin [Ansara and Dupin (1998)] for substitutional solutions according to the CALPHAD method:

$$\Delta_{mix}H = \sum_i \sum_{j>i} \left[x_i x_j \sum_\upsilon L_{i:j}^{(\upsilon)} (x_i - x_j)^\upsilon \right] \text{..(4.5)}$$

Where i and j are equal to 1 for Bi or 2 for In and $L_{i:j}^{(\upsilon)} (\upsilon = 0,1,2..)$ are the so called binary interaction parameters of the order υ . In this work equation (5.5) is the polynomial has the form:

$$\Delta_{mix}H = L_{1:2}^{(0)} x_1 x_2 + L_{1:2}^{(1)} x_1 x_2 (x_1 - x_2) + L_{1:2}^{(2)} x_1 x_2 (x_1 - x_2)^2 \text{ ....(4.6)}$$

Table 4.5 Interaction parameter for Bi-Sn, Bi-In and In-Sn systems

Interaction parameters	υ	(J/mol)
$L_{Bi\text{-}Sn}^{(\upsilon)}$ at 767 K	0	501
	1	232
	2	-150
	3	-148
$L_{Bi\text{-}Sn}^{(\upsilon)}$ at 813 K	0	520
	1	235
	2	-157
	3	-119
$L_{Bi\text{-}Sn}^{(\upsilon)}$ at 855 K	0	522
	1	244
	2	-101
	3	-151
$L_{Bi\text{-}In}^{(\upsilon)}$ at 767 K	0	-6760
	1	200
	2	1253
$L_{Bi\text{-}In}^{(\upsilon)}$ at 813 K	0	-6617
	1	133
	2	2066
$L_{Bi\text{-}In}^{(\upsilon)}$ at 855 K	0	-6417
	1	380
	2	2879
$L_{In\text{-}Sn}^{(\upsilon)}$ at 767 K	0	-2118
	1	-1077
$L_{In\text{-}Sn}^{(\upsilon)}$ at 813 K	0	-1980
	1	-893
$L_{In\text{-}Sn}^{(\upsilon)}$ at 855 K	0	-1854
	1	-725

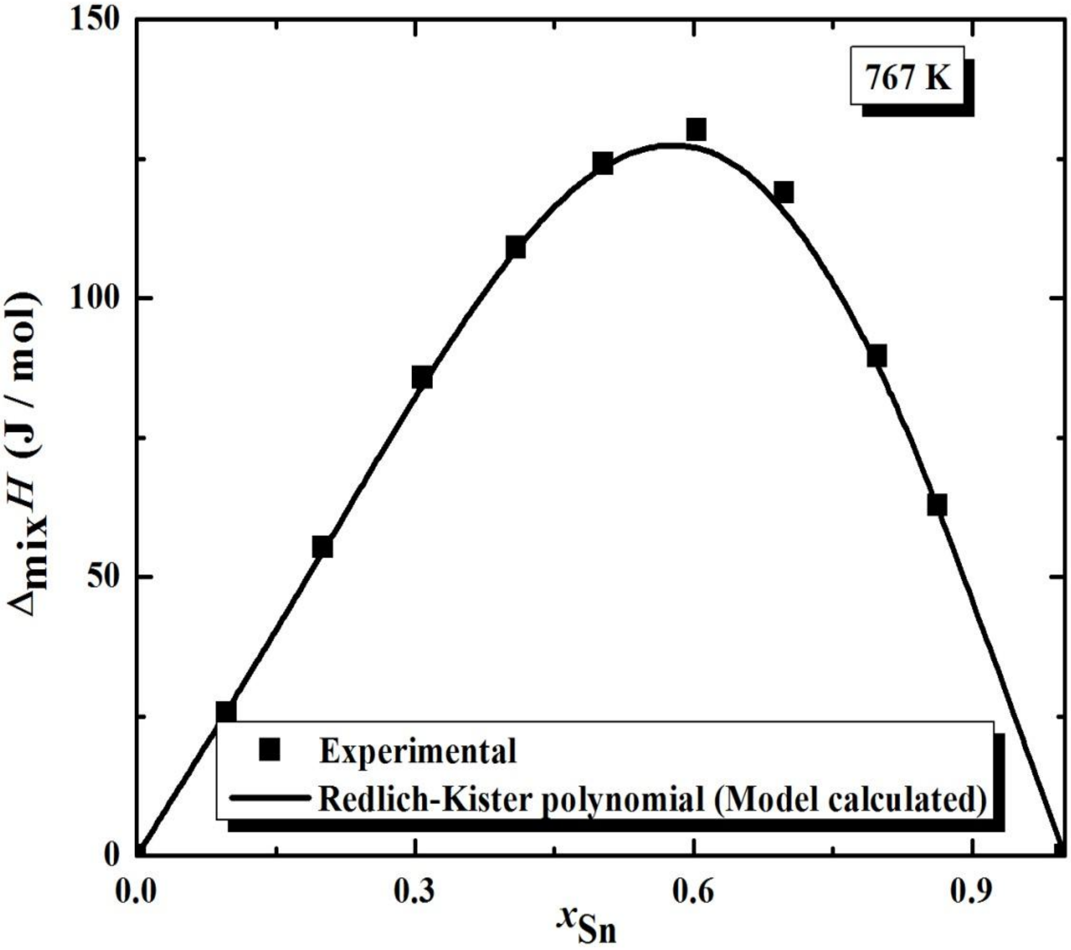

Figure 4.4 Comparison of Integral molar mixing enthalpies between theoretical model (Redlich-Kister Polynomial) and this experimental study at 767 K for Bi-Sn alloys

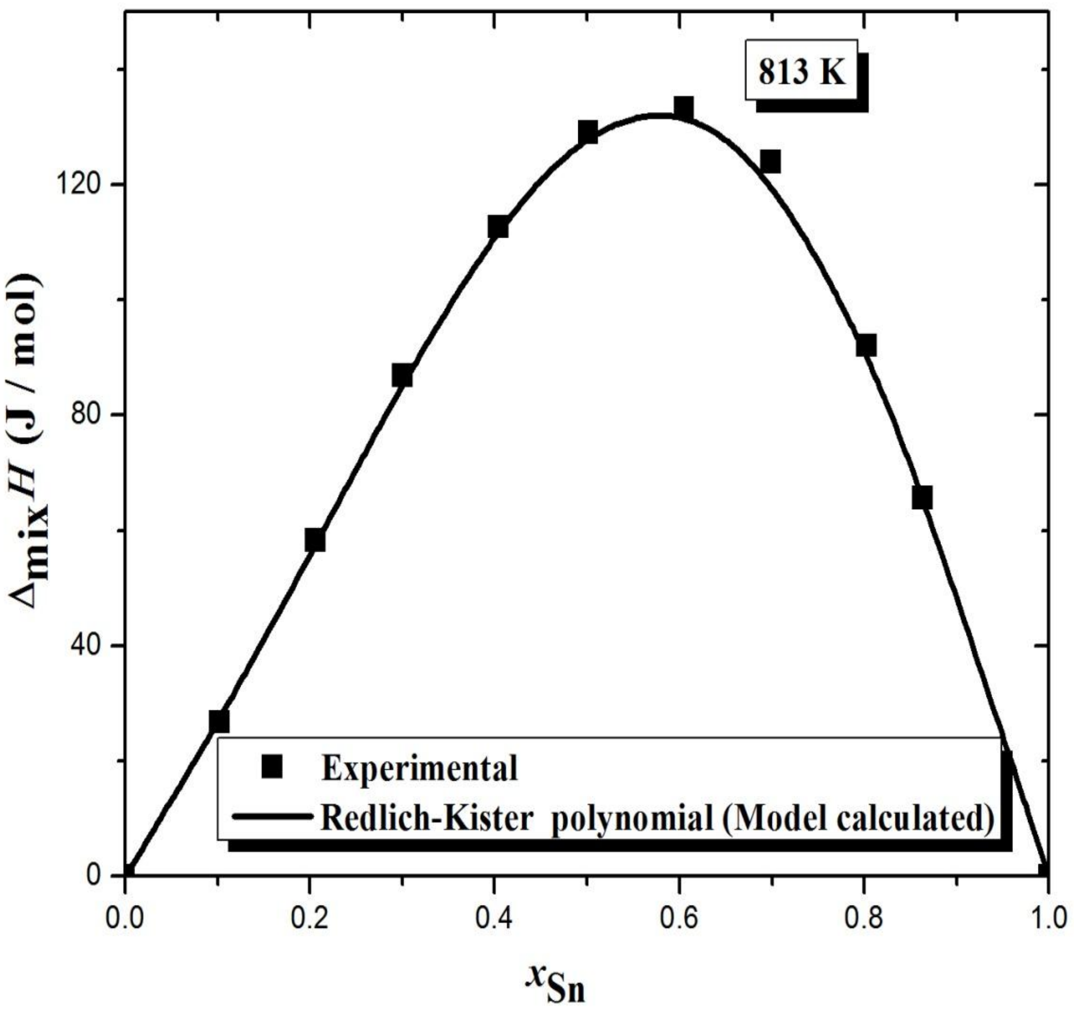

Figure 4.5 Comparison of Integral molar mixing enthalpies between theoretical model (Redlich-Kister Polynomial) and this experimental study at 813 K for Bi-Sn alloys

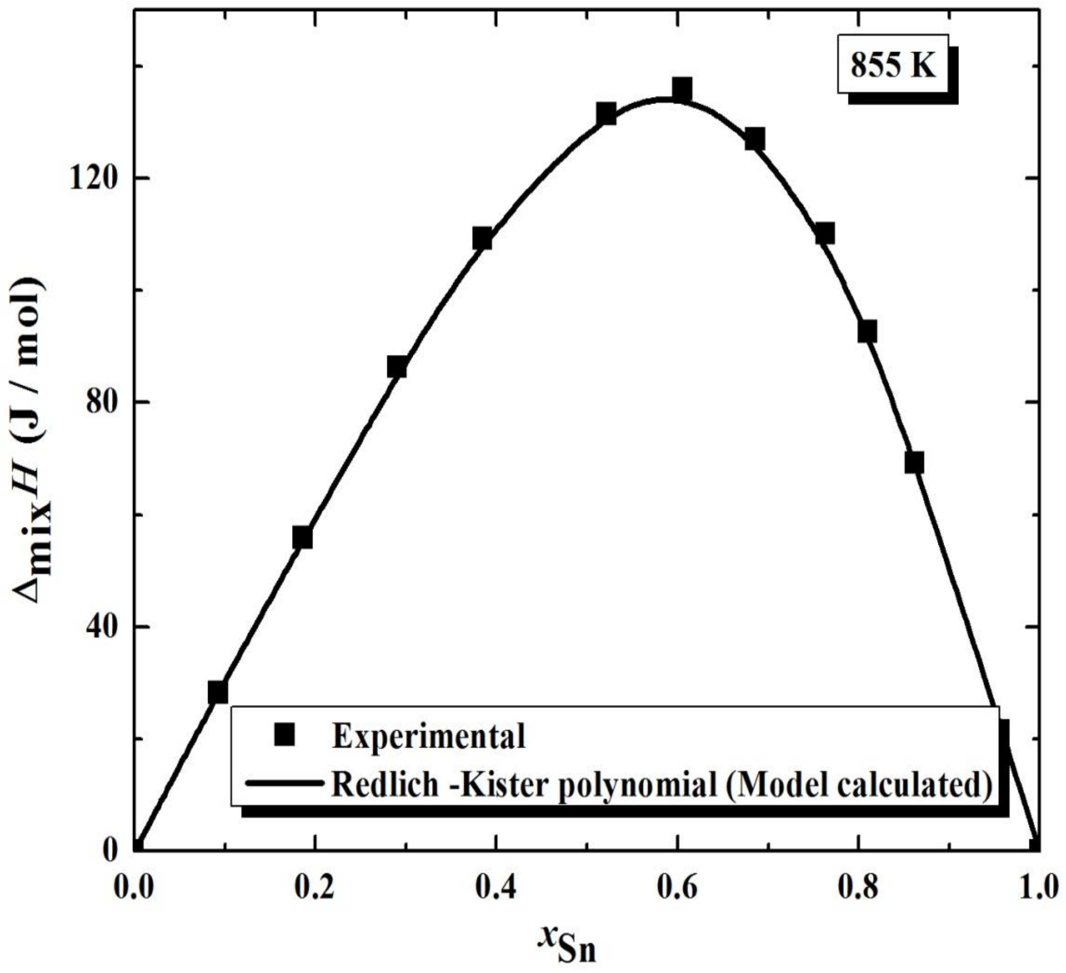

Figure 4.6 Comparison of Integral molar mixing enthalpies between theoretical model (Redlich-Kister Polynomial) and this experimental study at 855 K for Bi-Sn alloys

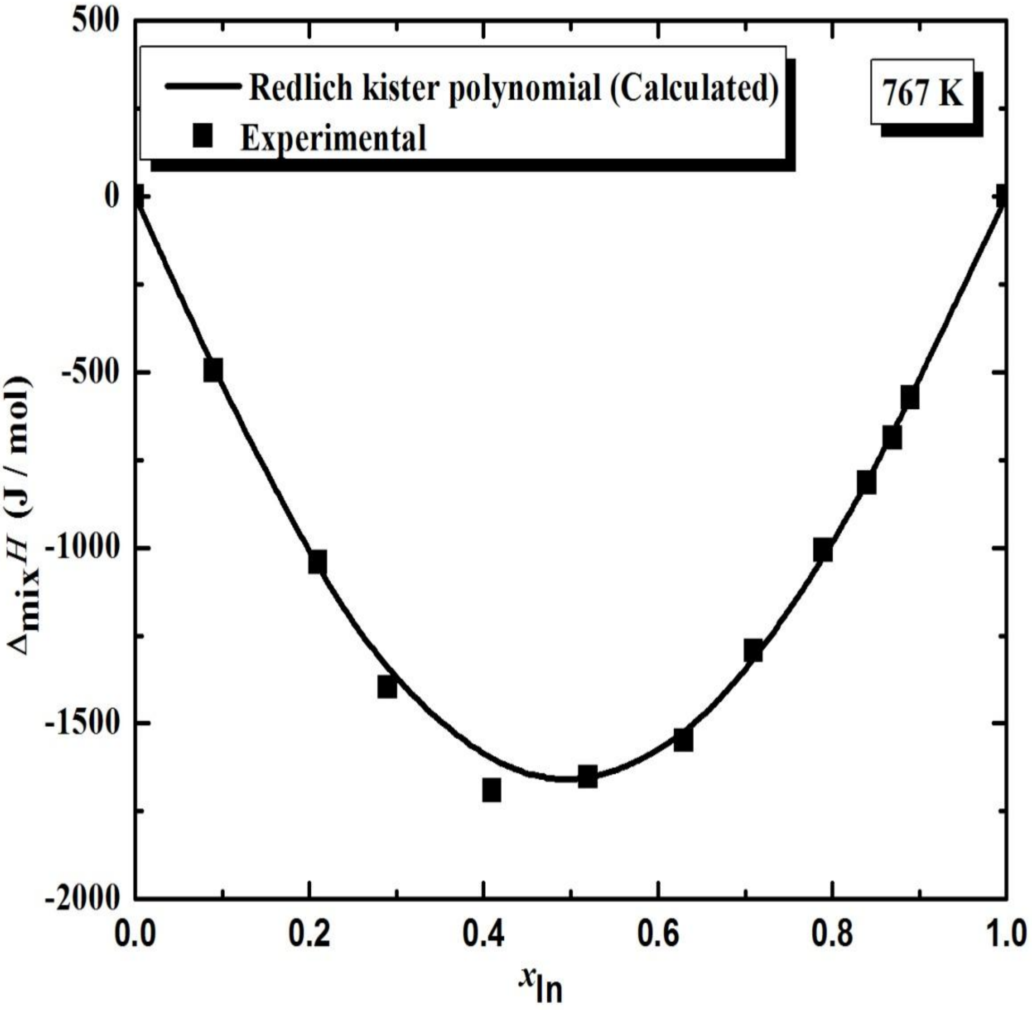

Figure 4.7 Comparison of Integral molar mixing enthalpies between theoretical model (Redlich-Kister Polynomial) and this experimental study at 767 K for Bi-In alloys

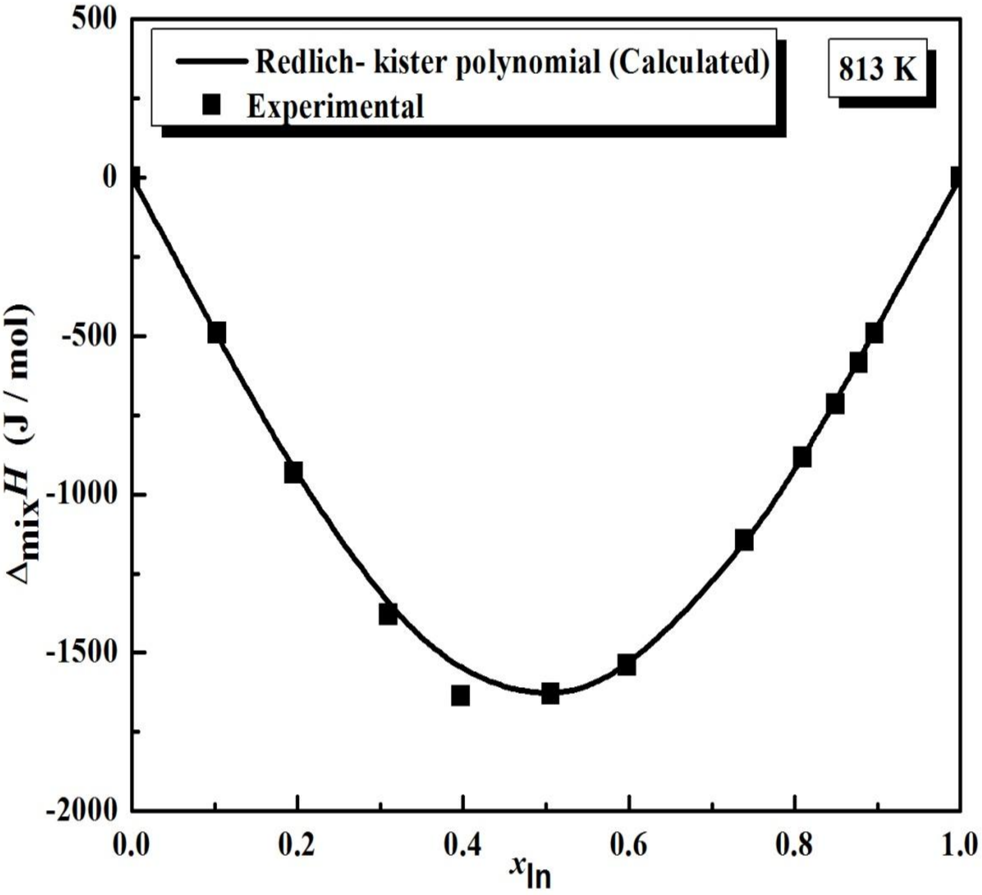

Figure 4.8 Comparison of Integral molar mixing enthalpies between theoretical model (Redlich-Kister Polynomial) and this experimental study at 813 K for Bi-In alloys

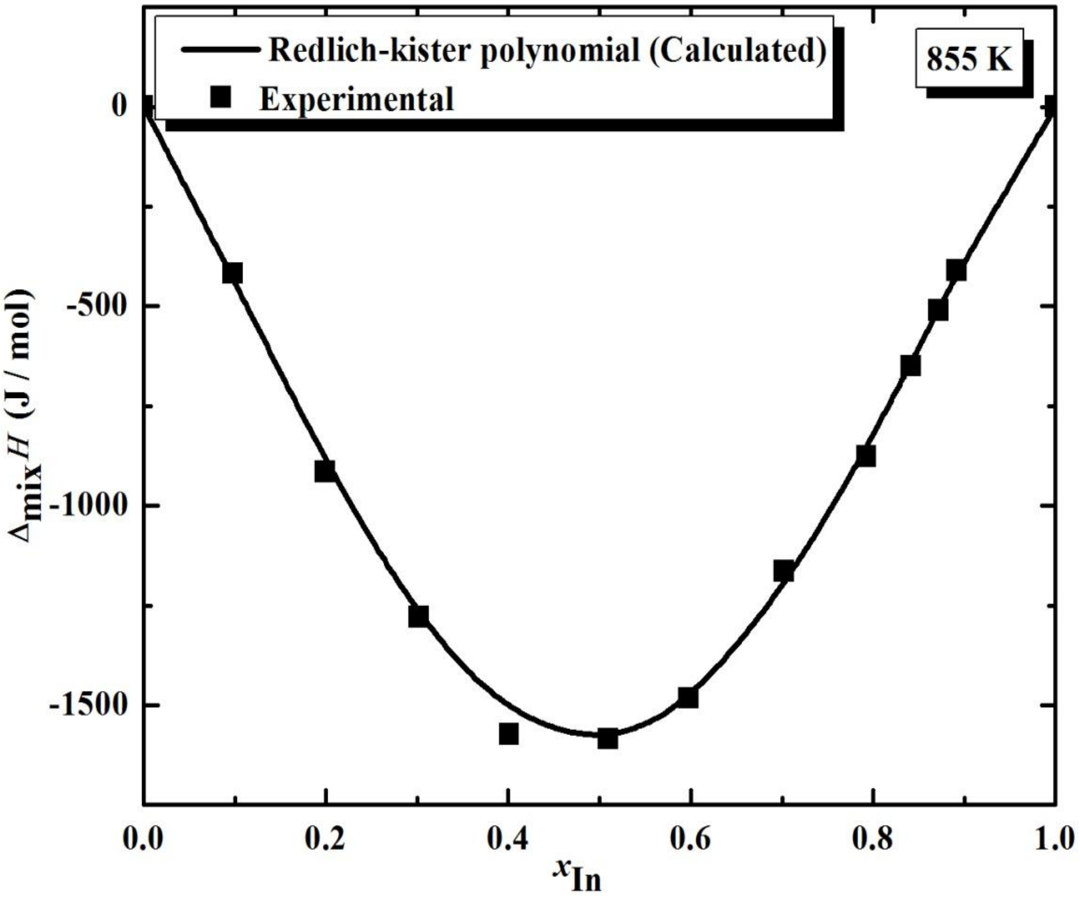

Figure 4.9 Comparison of Integral molar mixing enthalpies between theoretical model (Redlich-Kister Polynomial) and this experimental study at 855 K for Bi-In alloys

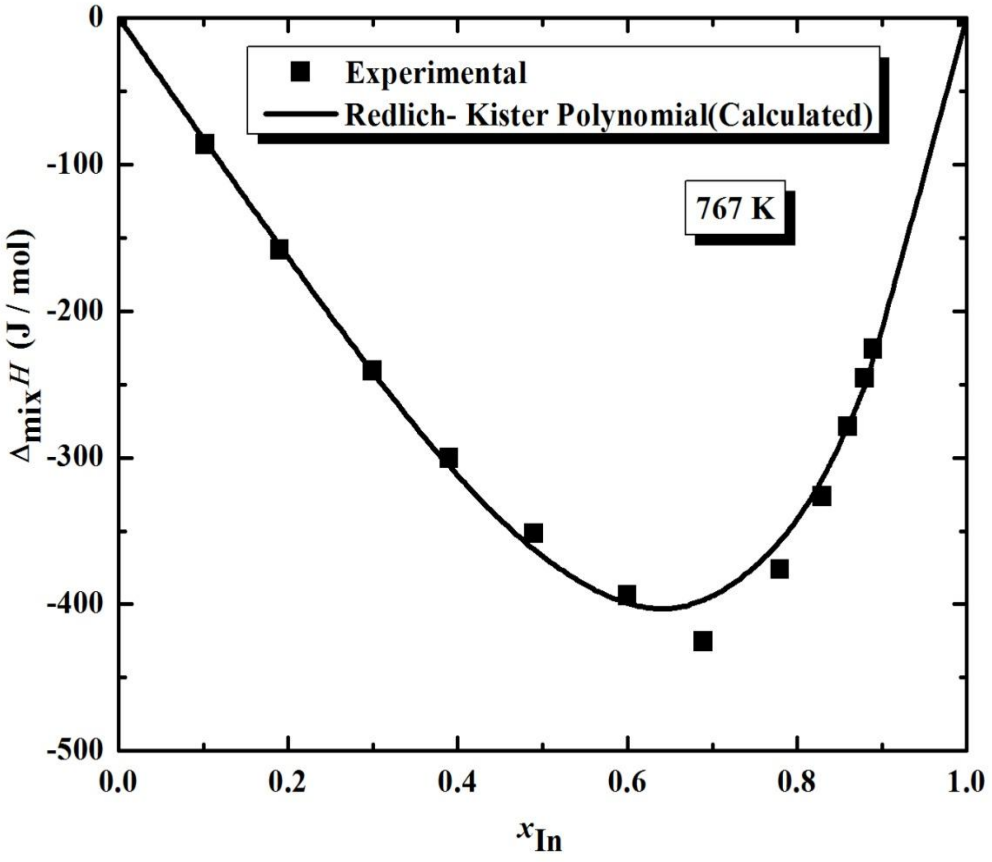

Figure 4.10 Comparison of Integral molar mixing enthalpies between theoretical model (Redlich-Kister Polynomial) and this experimental study at 767 K for In-Sn alloys

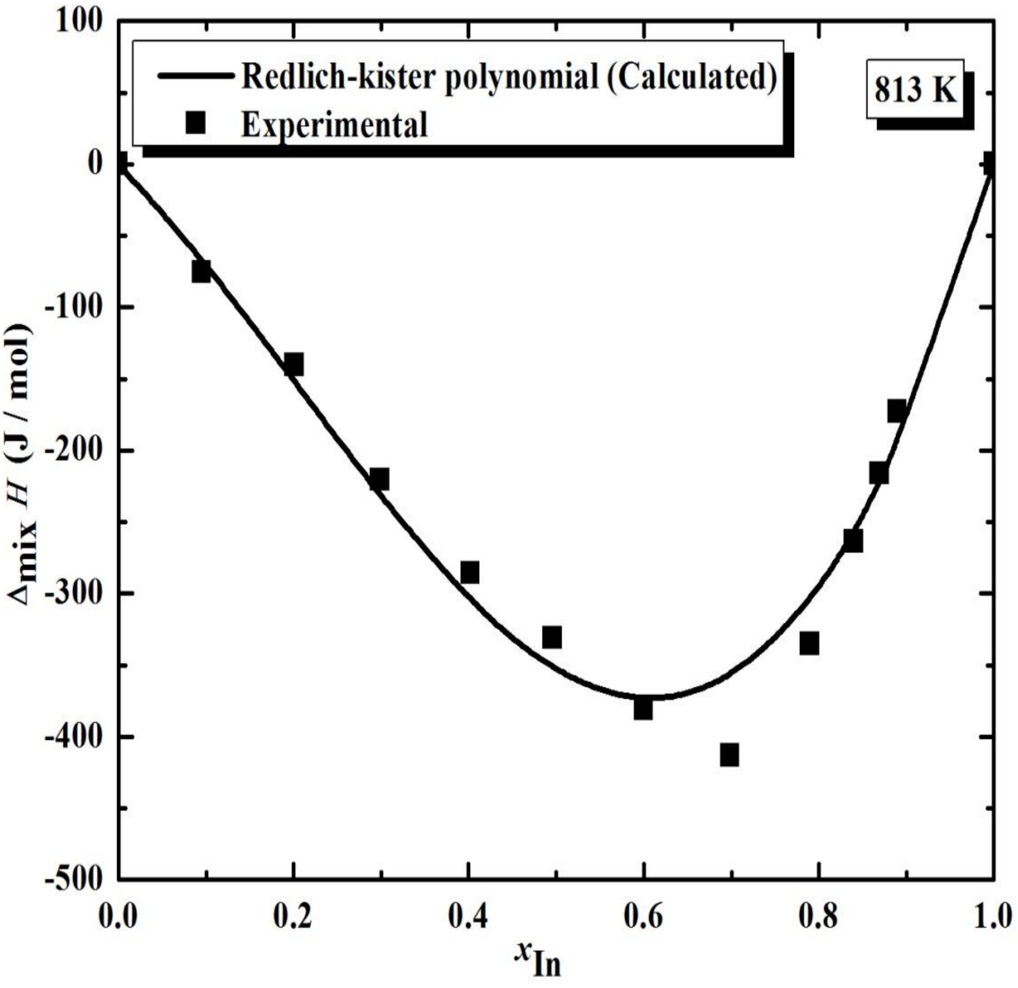

Figure 4.11 Comparison of Integral molar mixing enthalpies between theoretical model (Redlich-Kister Polynomial) and this experimental study at 813 K for In-Sn alloys

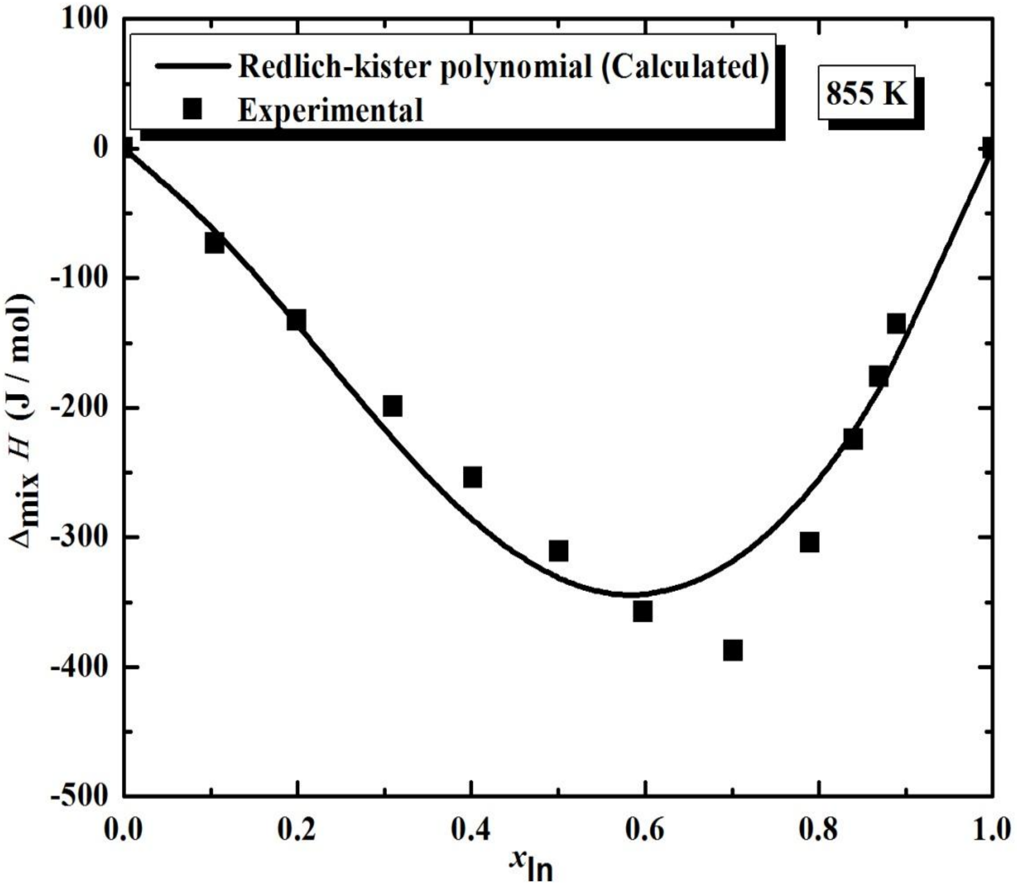

Figure 4.12 Comparison of Integral molar mixing enthalpies between theoretical model (Redlich-Kister Polynomial) and this experimental study at 855 K for In-Sn alloys

The experimental data are fitted with equation (4.6) as per the Redlich –Kister polynomial. To determine the function (ΔmixH/x_{Sn} X x_{Bi} J / mol) has been plotted with a function of composition difference correspondingly.

The cubic fitting equation of order three gives the best fit to the experimental data. Similarly it has done for various temperature i.e 767,813 and 855 K. The fitted parameters are called the binary interaction parameters. The interaction parameters are observed are presented in Table 4.5. A comparative study of the integral mixing enthalpy obtained experimentally and by the Redlich-Kister polynomial extrapolation is shown in Figures 4.4-4.12 and reveals good agreement with the experimental values for 767,813 and 855 K. It reveals that this measured data has more accuracy for all the compositions and can be used for multi component system.