3.1 Introduction

Lead-tin base solders have long been the most popular materials for electronic packaging because of their low cost and superior properties required for interconnecting electronic components. However, the toxic nature of lead and the increasing awareness of its adverse effect on environment and health have led to the pressing need for development of lead-free solders in recent years. Concern about the use of tin-lead solders in the electronics industry stems from occupational exposure, lead waste derived from the manufacturing process, and the disposal of electronic assemblies. It is now widely agreed that the main component of new lead free solders will be tin (e.g., Sn-Bi, Sn-In, Sn-Bi-In). One of the disadvantages of the above solder alloys is their higher melting point compared with the traditional tin-lead solders. Which creates some problems for the electronics industry; for one thing, the soldering processes would have to be adapted to higher temperatures; for another, all electronic devices, including the printed circuit boards, would have to be manufactured to withstand such higher soldering temperatures.

Thus it is quite serious and urgent reduce the melting temperature of the lead-free solder materials by alloying with additional elements, e.g. indium (mp 156.6^{o}C) as in the Bi-In-Sn system) Thermodynamic data are of great importance for the accurate calculation of phase diagrams, for the development of a lead-free solder database, for the design of new lead-free solders, and for the prediction of physical and chemical properties of lead-free solders, such as surface tension and viscosity. Therefore, it is necessary to study the thermodynamic properties of the ternary Bi-In-Sn system. Increased international demands and strong competitions make it necessary for the microelectronics and supporting industries to go for miniaturization of the product and produce more functional and reliable electronic products, economically. At the same

time, there is a serious concern of removing toxic elements, such as lead, from the electronic products. The classic lead-tin solder has been the unique solder materials for many years in these industries.

It has been a great challenge to develop lead-free solders that can be a suitable replacement for the conventional lead-tin eutectic solders. Simultaneously, there are strong demands for solders from various sectors like, avionics, automotive, military and oil exploration industries. Mostly, Properties related to manufacturability and reliability should be the initial criteria for the evaluation of lead-free solder candidate. The properties of the lead-free solders to be evaluated are: toxicity, cost, solidus temperature, oxidation resistance and flux compatibility. It has been observed that tin based alloys can satisfy the initial criteria to qualify for the high temperature lead-free solders. The exact determination of solidus and other physico-chemical properties will depend on the knowledge of phase equilibria and thermodynamic properties. So, the accurate determination the thermodynamic properties of the tin based ternary and higher order systems are very important.

The systematic thermodynamic investigations of multicomponent alloys are very important from the practical, scientific and technological point of view. The needs of physical and chemical data on the multicomponent solution have been growing enormously to develop new materials. Several objectives are achieved by the thermodynamic assessment of the multicomponent solutions. In the first place, they assist in the thermodynamic analyses of various metallurgical processes in which the multi component solutions take part. Second, thermodynamic data are required to ascertain the condition of the equilibrium between different phases. Third, thermodynamic data along with electrical, magnetic and X – ray investigations are essential to obtain a deeper insight into the constitution of a metallic system. The Bi -In

- Sn ternary system is one of the multi-component liquid alloys formed with low melting metals (Bismuth, indium, tin and lead). These alloys are always characterized by the low enthalpy of formation and no intermetallic compound. So the ternary Bi-In-Sn is used as one of the lead-free solder alloys.

3.2 Literature review

The phase diagram and thermodynamic properties of binary systems related to this ternary system are available in literatures [Boa (1998) and Seltz (1942)]. The thermodynamic properties of the In-Sn binary system were systematically studied by Vassiliev et.al. [Vassiliev et al. (1998)] in the temperature range of 636-820 K by the electromotive force measurement technique. The activity of the both components shows slightly negative deviations from Raoult's law in the complete range of composition.

Partial molar thermodynamic quantities of In and Bi in (xIn + (1 - x) Bi) (I) and excess thermodynamic propertied for the range of 673 to 873 K were measured by the emf technique using the concentration cells [Gregorczyk et al. (1981)]. The activities and relative enthalpies of tin and bismuth in their liquid alloys have been measured from electromotive force studies by Seltz and Dunkerly [Seltz and Dunkerley (1942)]. Behera and Shamsuddin [Behera and Shamsuddin (2009)] have determined the activity of zinc in the Zn-Sn-Ga system by EMF method in the temperature range 723-823 K. EMF measurements on the system In-Zn-Sn have been carried out by [Behera and Sonaye (2013)] in the temperature range 75 -853 K over three different sections. Torsion–effusion (T.E.) and Differential Scanning Calorimetry (DSC) techniques have been used to measure the Bi activity and mixing enthalpies in Bi-In-Sn system by Brunetti et al. [Brunetti et al. (2006)]. They have reported that the ternary system at fixed Bi composition, x_{Bi} = 0.20 at 565 K behaves as a non-ideal system with

exothermic $\Delta_{mix} H_T^o$ having a minimum at x_{In} = 0.58 and x_{Sn} = 0.22. The temperature of phase transition and enthalpy of melting of 29 different alloys from the Bi–In–Sn system were investigated by [Witusiewicz et al. (2007)] using DSC. Thermodynamic descriptions for the ternary systems Bi-In-Sn, Bi-In-Zn, Bi-Sn-Zn and In-Sn-Zn were optimized using CALPHAD method and combined to obtain a description of the quaternary Bi-In-Sn-Zn system by Moleans et al. [Moelans et al. (2003)]. Partial and Integral quantities as well as the activity and the excess Gibbs free energy of the ternary Bi-In-Zn system have been determined at 873K with the emf method at liquidus temperature and 973 K [Knott et al. (2010)].

From the literature survey we observed that no investigations on In-Sn-Bi system has been carried out using electrochemical measurement technique and very limited data on thermodynamic properties is available in the literature so, this chapter describes the electrochemical study of Bi -In-Sn ternary metallic system in the liquid phase and utilizes the Darken's method to determine the integral and partial molar free energy, heat and entropy of solution. The thermodynamic properties of Indium along different cross sections in the ternary fields in the Bi-In-Sn system were evaluated from the measured data. Various excess molar and excess partial molar thermodynamic properties of the three components were computed at 813 K.

The aim of this study is to measure the activity of indium along constant x_{Bi}/x_{Sn} ratios of 0.5, 1 and 2 by EMF technique using molten salt electrolyte in the temperature range of 723-855K. The activity of tin in Bi-Sn binary system is also measured by same technique in the same temperature range. Various thermodynamic properties are calculated using Darken Treatments for multicomponent solutions from the measured activity of In in Bi-In-Sn system and thermodynamic properties of Bi-Sn binary system. Isoactivity of indium and isoexcess free energy in Bi-In-Sn system are plotted

at 813 K. The ternary excess free energy will be calculated from the activity data using Darken's treatment of ternary systems. The calculated ternary excess free energy will be compared with the theoretical model assessment. The ternary excess free energy surface will be presented to demonstrate the orientation of the stability of phases in the ternary systems at 813 K. An effort were made to compare the excess molar free energy between Muggianu model and this study at 813 K for $Bi_{0.33}Sn_{0.67}$-In alloy.

3. 3 Experimental

3. 3. 1 Electrochemical Measurement

The activity of In in the liquid Bi-In-Sn system was determined in the temperature range 723-855 K by measuring the reversible open circuit electromotive force (emf) of the following electrochemical cell:

$$In\ (l)\ \left|\ LiCl - KCl + 5\ wt.\ pct\ InCl\ \right|\ In_x\,(Sn_y\ Bi_{1-y})_{1-x}\ (1) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ (3.\ 1)$$

The compositions of the ternary alloys were selected for different sections as Inx $(Sn_y\ Bi_{1-y})_{1-x}$, where y = 0.33, 0.50 and 0.67 and x = 0.1, 0.3, 0.5, 0.7 and 0.9 as shown in Figure 3.1. The electrolyte used for this study consists of eutectic mixture of LiCl-KCl containing 5 wt. % InCl. A cell assembly made of BOROSIL glass containing six lower limbs (6 mm internal diameter each) below a tubular electrolyte compartment (60 mm internal diameter) was used in this investigation. At the bottom of each limb, an electrode contact wire of tungsten (0.4 mm diameter and 20 cm length) was sealed. The preparation of electrolyte, design of the cell assembly and experimental techniques of equilibrium measurement of the cell emf has been described in detail in Chapter 2. The experiments were performed in three steps involving different compositions of $(Sn_{0.33}Bi_{0.67})_{1-x}\ In_x$ liquid solutions. The first step involved compositions and x = 0.1, 0.3, 0.5, 0.7 and 0.9. In the second step, $(Sn_{0.50}Bi_{0.50})_{1-x}\ In_x$ and x = 0.1, 0.3, 0.5, 0.7 and

0.9 and third step involved $(Sn_{0.67}Bi_{0.33})_{1-x}$ In_x and x = 0.1, 0.3, 0.5, 0.7 and 0.9. In all the three cases, pure indium was used as a reference electrode in one of the six limbs and rests of the five limbs contained the ternary alloys of different compositions. The emf of the galvanic cell was measured during heating as well as cooling cycles. Investigations on each composition were repeated to check the reproducibility of the results.

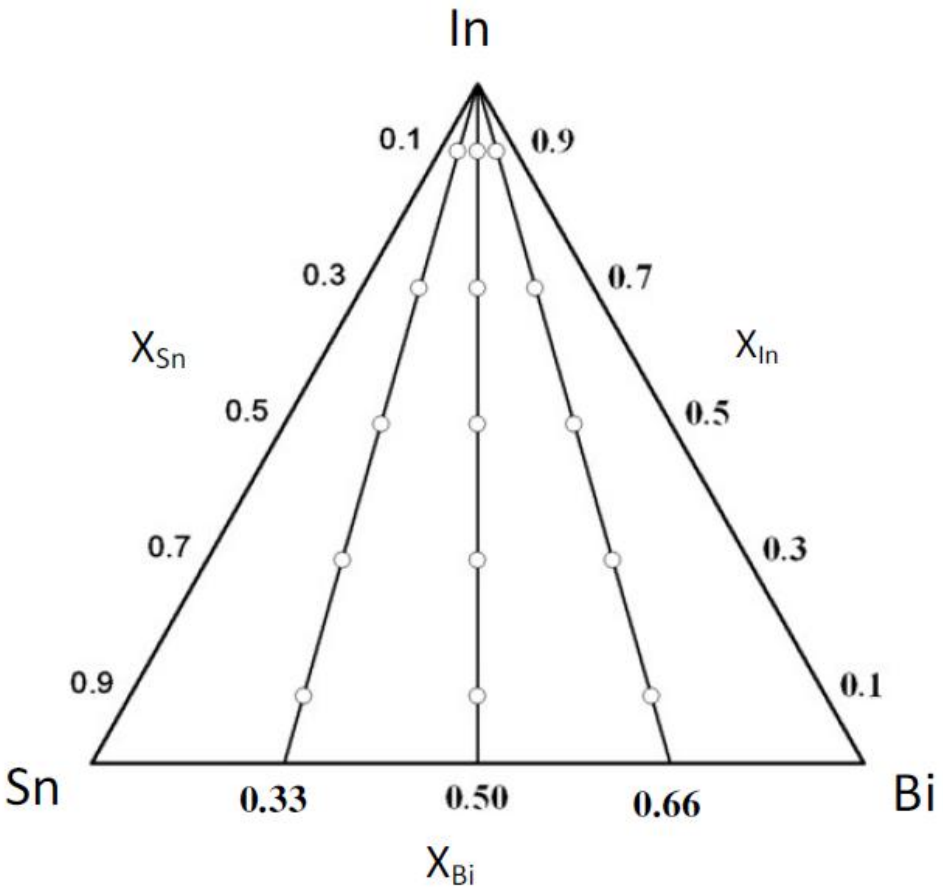

Figure 3.1 Composition selected for activity measurement

A maximum weight of 3 gm was decided and the weights of the individual components were calculated based on the mole fractions. These are reproduced in Table 3.1

Table 3.1 Weights in gm of all components

X_{Sn}/X_{Bi}	Mole Fraction			Molecular weight (gm)			Total Weight (gm)	Weight of individual component (gm)		
	x_{In}	x_{Sn}	x_{Bi}	In	Sn	Bi		W(In)	W(Sn)	W(Bi)
0.5	0.1	0.300	0.600	114.818	118.71	208.98	3	0.199703	0.61942	2.180879408
	0.3	0.233	0.467	114.818	118.71	208.98		0.647192	0.52043	1.832373889
	0.5	0.167	0.333	114.818	118.71	208.98		1.172776	0.40418	1.423047379
	0.7	0.100	0.200	114.818	118.71	208.98		1.798854	0.26569	0.935456066
	0.9	0.033	0.067	114.818	118.71	208.98		2.557294	0.09793	0.344780353
1	0.1	0.450	0.450	114.818	118.71	208.98	3	0.216716	1.00828	1.775003945
	0.3	0.350	0.350	114.818	118.71	208.98		0.692894	0.83578	1.471327373
	0.5	0.250	0.250	114.818	118.71	208.98		1.236094	0.639	1.124908424
	0.7	0.150	0.15	114.818	118.71	208.98		1.861538	0.41242	0.726040000
	0.9	0.050	0.050	114.818	118.71	208.98		2.589431	0.14873	0.261834854
2	0.1	0.600	0.300	114.818	118.71	208.98	2.5	0.197415	1.22464	1.077945129
	0.3	0.467	0.233	114.818	118.71	208.98		0.621285	0.9992	0.879512225
	0.5	0.333	0.167	114.818	118.71	208.98		1.088867	0.75052	0.660615865
	0.7	0.200	0.100	114.818	118.71	208.98		1.607289	0.47479	0.417918507
	0.9	0.067	0.033	114.818	118.71	208.98		2.185322	0.16736	0.147315087

3.4 Results and discussion

3. 4. 1 Activity of indium

The net cell reaction in the galvanic cell (3. 1) is be represented as follows:

In (pure) → in (in Bi-In-Sn) ..... (3. 2)

The activity of Indium in the Bi-In-Sn system was calculated from the equation (1.12). The reversible emf values, measured in the temperature range 723-855 K, are listed in Table 3. 2. The variation of emf a function of temperature for fifteen different compositions was calculated by the least square method and is presented in Table 3. 2 in the form of a linear equation (E = A + BT). The error limit shown in the Table 3.2 and Figures 3.2a, 3.2b and 3. 2c are the maximum deviations from the average value of cell emf from two independent runs.

From the emf values measured at different temperatures presented inTable 3.2, activity of Indium in Bi-In-Sn liquid alloys was calculated from equation (1. 15) and the calculated values are listed in Table 3.5 The corresponding values of the activity coefficient of Indium (γ_{In}) calculated from equation:

$$\gamma_{In} = \frac{a_{In}}{x_{In}} \quad \text{..... (3. 3)}$$

Table 3.2 Galvanic cell measured EMF ((mv) for Bi-In-Sn alloys

Galvanic cell EMF(mv) at different Temp											
$(Sn_{0.33}Bi_{0.67})_{1-x}$ In_x		Temperature K							E=A+BT	
x_{In}	x_{Sn}/x_{Bi}	723	745	767	789	813	833	855	(-A)	(B)
0.1	0.5	215.870(±3.894)	221.155(±3.981)	227.899(±4.102)	233.944(±4.679)	240.457(±4.809)	247.134(±5.661)	253.879(±5.828)	12.352	0.281
0.3		180.657(±3.432)	183.805(±3.492)	188.953(±3.590)	194.101(±4.076)	199.717(±4.194)	205.397(±4.519)	210.545(±4.632)	11.385	0.232
0.5		148.759(±2.961)	151.336(±3.027)	154.612(±3.092)	159.889(±3.518)	164.555(±3.620)	169.443(±3.897)	172.72(±3.973)	9.451	0.191
0.7		65.517(±1.365)	66.887(±1.405)	68.258(±1.433)	70.328(±1.688)	72.668(±1.744)	73.368(±1.834)	76.738(±1.931)	5.336	0.0826
0.9		4.080(±0.045)	4.181(±0.046)	4.230(±0.047)	4.293(±0.052)	4.338(±0.052)	4.384(±0.048)	4.535(±0.050)	1.894	0.00304
$(Sn_{0.50}Bi_{0.50})_{1-x}$ In_x		Temperature(K)							E=A+BT	
x_{In}	x_{Sn}/x_{Bi}	723	745	767	789	813	833	855	(-A)	(B)
0.1	1	247.581(±6.932)	251.787(±7.050)	257.993(±7.224)	265.200(±6.100)	270.970(±6.232)	276.612(±8.022)	284.318(±8.245)	44.249	0.279
0.3		137.296(±3.432)	140.303(±3.508)	144.010(±3.600)	147.317(±3.388)	150.597(±3.464)	152.33(±4.570)	155.337(±4.660)	38.409	0.137
0.5		59.528(±1.310)	61.137(±1.349)	62.597(±1.377)	63.457(±1.523)	65.258(±1.566)	65.982(±1.650)	66.833(±1.671)	20.236	0.0549
0.7		22.512(±0.450)	22.902(±0.458)	23.492(±0.470)	24.181(±0.532)	24.725(±0.544)	25.261(±0.581)	26.250(±0.604)	2.280	0.02776
0.9		2.997(±0.036)	3.094(±0.037)	3.191(±0.038)	3.288(±0.036)	3.393(±0.037)	3.502(±0.046)	3.558(±0.046)	-0.161	0.00437
$(Sn_{0.67}Bi_{0.33})_{1-x}$ In_x		Temperature (K)							E=A+BT	
x_{In}	x_{Sn}/x_{Bi}	723	745	767	789	813	833	855	(-A)	(B)
0.1	2	168.055(±3.361)	171.385(±3.428)	174.114(±3.482)	178.844(±4.113)	183.913(±4.230)	186.304(±4.658)	190.034(±4.751)	44.008	0.1709
0.3		101.282(±2.228)	103.171(±2.270)	105.961(±2.331)	108.050(±2.701)	109.702(±2.743)	110.829(±2.992)	112.118(±3.027)	41.399	0.0835
0.5		57.665(±1.326)	58.604(±1.348)	60.244(±1.386)	61.884(±1.547)	63.672(±1.592)	65.363(±1.765)	67.303(±1.817)	3.554	0.07418
0.7		30.509(±0.671)	31.128(±0.685)	32.327(±0.711)	32.927(±0.856)	33.908(±0.882)	34.925(±0.803)	35.875(±0.825)	0.825	0.0408
0.9		3.309(±0.046)	3.448(±0.048)	3.536(±0.050)	3.620(±0.058)	3.715(±0.059)	3.845(±0.069)	3.955(±0.071)	0.0803	0.0047

$x_{Sn,}$ $x_{Bi,}$ $x_{In}$is the mole fraction of tin,bismuth and indium respectively. A and B are the slope and intercept of the line *E vs. T.*

Table 3.3 Galvanic cell electromotive force *E* (millivolt) at different temperature *T* for Bi- Sn system

x_{Sn}	EMF(mV)			
	723 K	**773 K**	**813 K**	**855 K**
0.897	3.212(±0.098)	3.428 (± 0.101)	3.598(±0.108)	3.883(±0.115)
0.758	8.295(±0.253)	8.921(±0.31)	9.405(±0.329)	10.003(±0.349)
0.705	10.701(±0.412)	11.440(±0.457)	12.051(±0.482)	12.647(±0.507)
0.599	15.200(±0.684)	16.290(±0.73)	17.221(±0.775)	18.154 (±0.820)
0.501	21.186(±0.857)	22.776 (±1.133)	23.988 (±1.199)	25.295(±1.265)
0.405	27.417(±1.453)	29.437(±1.608)	30.993(±1.705)	32.622(±1.801)
0.297	37.230(±1.263)	40.07(±1.568)	42.222 (±1.667)	44.302(±1.449)
0.199	49.595(±1.726)	53.102 (±1.986)	56.043(±1.994)	59.200(±1.895)
0.106	68.952(±1.986)	73.852(±2.123)	78.112 (±2.45)	82.060(±2.394)

Table3.4 Activity for Bi-Sn system

x_{Sn}	a_{Sn}			
	723 K	**773 K**	**813 K**	**855 K**
0.897	$0.902(\pm 8.8\times10^{-5})$	$0.902(\pm 8.8\times10^{-5})$	$0.902(\pm 8.8\times10^{-5})$	$0.900(\pm 8.8\times10^{-5})$
0.758	$0.766(\pm\times10^{-4})$	$0.765(\pm\times10^{-4})$	$0.765(\pm\times10^{-4})$	$0.762(\pm\times10^{-4})$
0.705	$0.709(\pm\times10^{-4})$	$0.709(\pm\times10^{-4})$	$0.709(\pm\times10^{-4})$	$0.709(\pm\times10^{-4})$
0.599	$0.614(\pm\times10^{-4})$	$0.613(\pm\times10^{-4})$	$0.612(\pm\times10^{-4})$	$0.611(\pm\times10^{-4})$
0.501	$0.507(\pm\times10^{-4})$	$0.505(\pm\times10^{-4})$	$0.504(\pm\times10^{-4})$	$0.503(\pm\times10^{-4})$
0.405	$0.415(\pm\times10^{-4})$	$0.413(\pm\times10^{-4})$	$0.413(\pm\times10^{-4})$	$0.412(\pm\times10^{-4})$
0.297	$0.303(\pm\times10^{-4})$	$0.300(\pm\times10^{-4})$	$0.300(\pm\times10^{-4})$	$0.300(\pm\times10^{-4})$
0.199	$0.203(\pm\times10^{-4})$	$0.203(\pm\times10^{-4})$	$0.202(\pm\times10^{-4})$	$0.200(\pm\times10^{-4})$
0.106	$0.109(\pm\times10^{-4})$	$0.109(\pm\times10^{-4})$	$0.108(\pm\times10^{-4})$	$0.108(\pm\times10^{-4})$

[a] x_{Sn} is the mole fraction of tin and a_{Sn} is the activity of tin. Pressure (P) = 999 hPa. Standard uncertainty u (P) = 2hPa, u (T) = 1K and u (x_{Sn}) = 0.001.

Table 3.5 Activity of Indium (a_{In}) in Bi-In-Sn alloys

		Temperature K					
	x_{Sn}/x_{Bi}	723	745	767	789	813	833	855
x_{In}								
0.1	0.5	0.03127	0.03191	0.03180	0.03203	0.03231	0.03197	0.03188
0.3		0.05504	0.05709	0.05733	0.05756	0.05800	0.05700	0.05700
0.5		0.09184	0.09467	0.09639	0.09500	0.09500	0.09400	0.09600
0.7		0.34937	0.35278	0.35600	0.35500	0.35400	0.36000	0.35290
0.9		0.93661	0.93700	0.93800	0.93900	0.94000	0.94100	0.94030

$(Sn_{0.50}Bi_{0.50}$		Temperature(K)						
x_{In}	x_{Sn}/x_{Bi}	723	745	767	789	813	833	855
0.1	1	0.0188	0.01980	0.02017	0.02023	0.02090	0.02120	0.02109
0.3		0.11039	0.11242	0.11316	0.11454	0.11700	0.12000	0.12100
0.5		0.38462	0.38472	0.38786	0.39300	0.39400	0.39900	0.40400
0.7		0.69674	0.69995	0.70100	0.70100	0.70300	0.70300	0.70000
0.9		0.95303	0.95300	0.95300	0.95300	0.95300	0.95200	0.95285

$(Sn_{0.67}Bi_{0.33}$		Temperature (K)						
x_{In}	x_{Sn}/x_{Bi}	723	745	767	789	813	833	855
0.1	2	0.06738	0.06927	0.07176	0.07204	0.07242	0.07461	0.07582
0.3		0.19677	0.20046	0.20125	0.20408	0.20900	0.21352	0.21800
0.5		0.39630	0.40136	0.40191	0.40200	0.40298	0.40200	0.40100
0.7		0.61281	0.61577	0.61300	0.61613	0.61600	0.61500	0.61500
0.9		0.94828	0.94800	0.94790	0.94800	0.94800	0.94800	0.94774

x_{In}, x_{Bi}, x_{Sn} is the mole fraction of indium,bismuth and tin respectively in the ternary alloys.

are also presented in Table 3.6 at different temperatures and represented in the form of linear equation. The activity and activity co-efficient both decrease with increase of temperature. Activity as a function of composition at a given temperature of 813 is presented in Figure 3.3 The activity of indium in In-Sn-Bi alloys shows negative deviation from Raoult's law for most of the compositions and slight positive deviations for a few indium-rich compositions. The plot exhibits strong negative deviations from Raoult's law for the two of the ternary sections (x_{Sn}/x_{Bi} = 1 and 2). The values obtained for the third ternary section (x_{Sn}/x_{Bi} = 0.5) are not interpretable due to attainment of equilibrium reflected from the unstable emf values. The negative deviation from the Raoult's law clearly indicates that there is attractive interaction between In, Sn and Bi atoms.

The isoactivity curves of indium in liquid Bi-In-Sn alloys were derived from the activity values for liquid Bi-In and In-Sn alloys as the starting and ending points and the experimental results for the ternary alloys are used. From the smoothing of curves of a_{In} vs x_{In} plots in each binary and ternary system, the alloy compositions corresponding to the activity values of the every one tenth were read. The isoactivity curves at 813K are shown in Figure 3.4. Each curve in ternary alloys region represents that near In-Bi line deviation from ideality is highly negative and near In-Sn curve, it shows approximately ideal behavior. The solubility of indium in the ternary alloy increases with the addition of indium. There is no chance of phase separation in the indium rich alloys. Which indicates the tendency of clustering of In and Bi in the second nearest neighborhood.

Table 3.6 Activity coefficient of Indium (γ_{In}) in Bi-In-Sn alloys

$(Sn_{0.33}Bi_{0.67}$		Temperature K						
x_{In}	x_{Sn}/x_{Bi}	723	745	767	789	813	833	855
0.1	0.5	0.31270	0.31910	0.3180	0.32030	0.32310	0.31970	0.31880
0.3		0.18346	0.19030	0.19110	0.19186	0.19333	0.19000	0.19000
0.5		0.18368	0.18934	0.19278	0.19000	0.19000	0.18800	0.19200
0.7		0.49910	0.50397	0.50857	0.50714	0.50571	0.51428	0.50414
0.9		1.04067	1.04111	1.04222	1.04333	1.04444	1.04555	1.04477

$(Sn_{0.50}Bi_{0.50})_{1-}$		Temperature(K)						
x_{In}	x_{Sn}/x_{Bi}	723	745	767	789	813	833	855
0.1	1	0.18800	0.19800	0.20170	0.20230	0.20900	0.21200	0.21090
0.3		0.36796	0.37473	0.37720	0.38180	0.39000	0.40000	0.40333
0.5		0.76924	0.76944	0.77572	0.78600	0.78800	0.79800	0.80800
0.7		0.99534	0.99992	1.00142	1.00142	1.00428	1.00428	1.01020
0.9		1.05892	1.05888	1.05888	1.05888	1.05888	1.05777	1.05872

$(Sn_{0.67}Bi_{0.33})_{1-}$		Temperature (K)						
x_{In}	x_{Sn}/x_{Bi}	723	745	767	789	813	833	855
0.1	2	0.67380	0.69270	0.71760	0.72040	0.72420	0.74610	0.75820
0.3		0.65590	0.66820	0.67083	0.68026	0.69666	0.71173	0.72666
0.5		0.79260	0.80272	0.80382	0.80400	0.80596	0.80400	0.80200
0.7		0.87544	0.87967	0.87571	0.88018	0.88000	0.87857	0.87857
0.9		1.05364	1.05333	1.05322	1.05333	1.05333	1.05333	1.05304

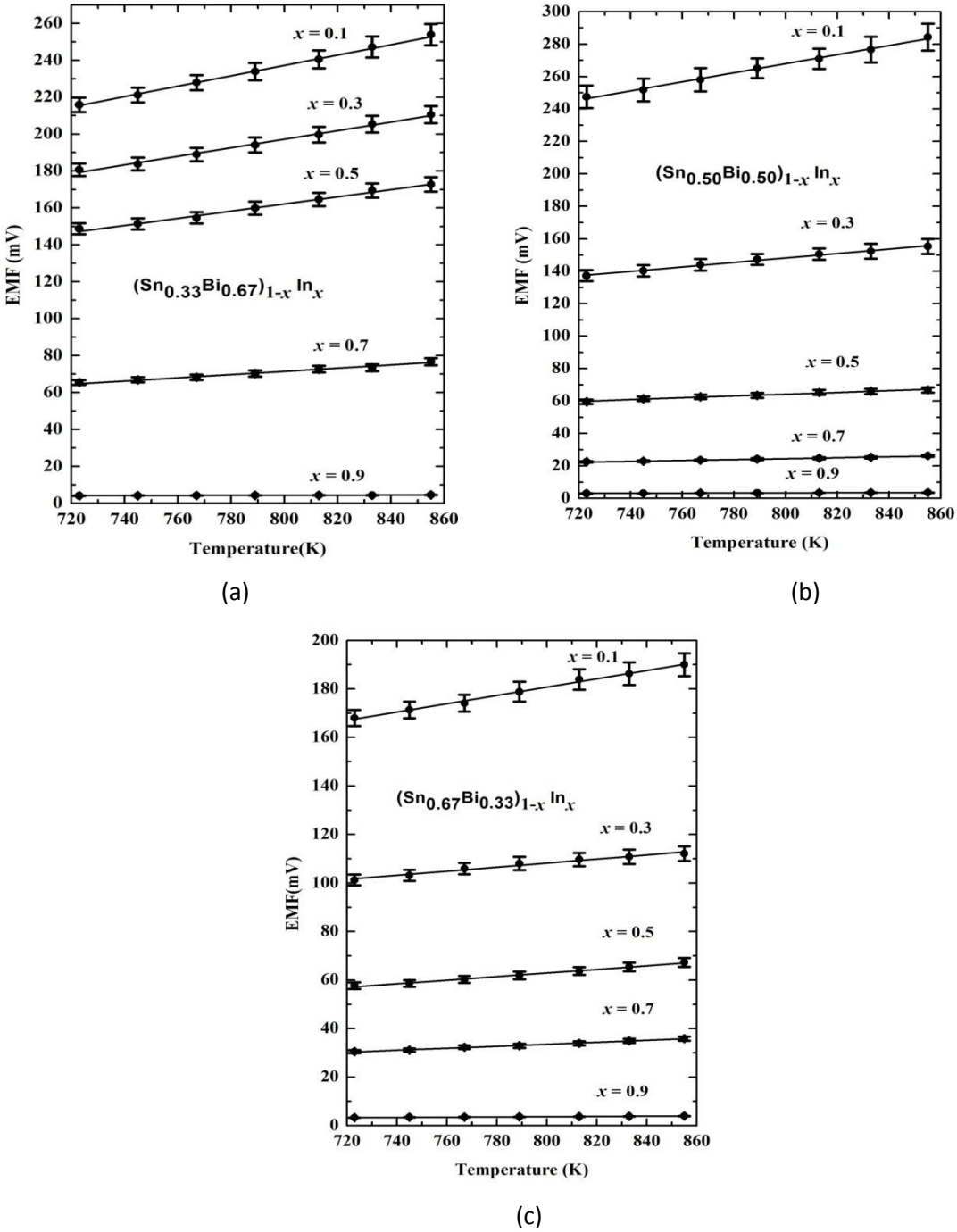

Figure 3.2 EMF vs Temperature plot of Galvanic cell a**)** in (l) |KCl-LiCl|In_x $(Sn_{0.33}$ $Bi_{0.67})_{1-x}$ (l) b) In (l) |KCl-LiCl|In_x $(Bi_{0.5}Sn_{0.5})_{1-x}$ (l) and c) In (l) | KCl-LiCl | In_x $(Sn_{0.67}$ $Bi_{0.33})_{1-x}$ (l)

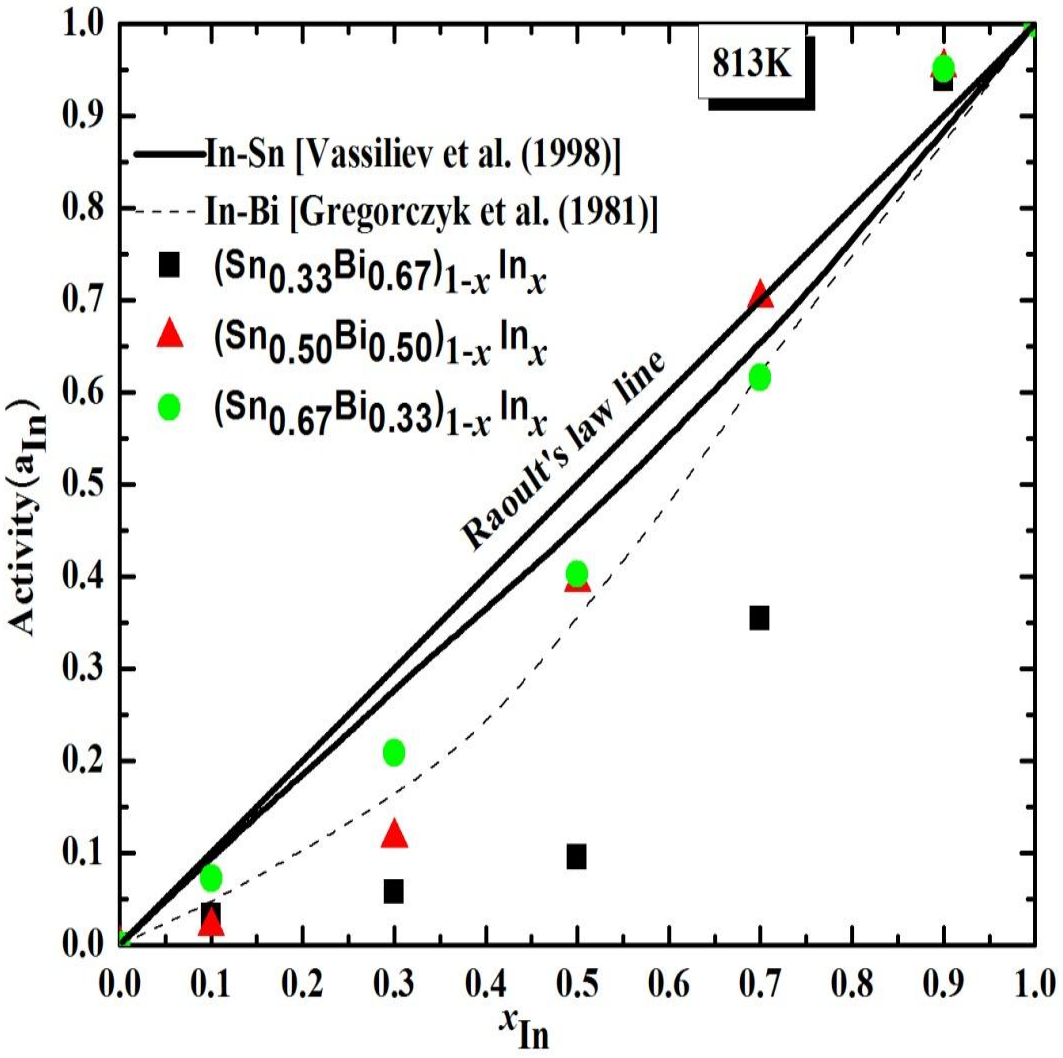

Figure 3.3 Activity of Indium in In-Sn,In-Bi and $(Sn_{0.33}Bi_{0.67})_{1-x}\ In_x$; ■, $(Sn_{0.50}Bi_{0.50})_{1-x}\ In_x$; ▲ and $(Sn_{0.67}Bi_{0.33})_{1-x}\ In_x$; ●

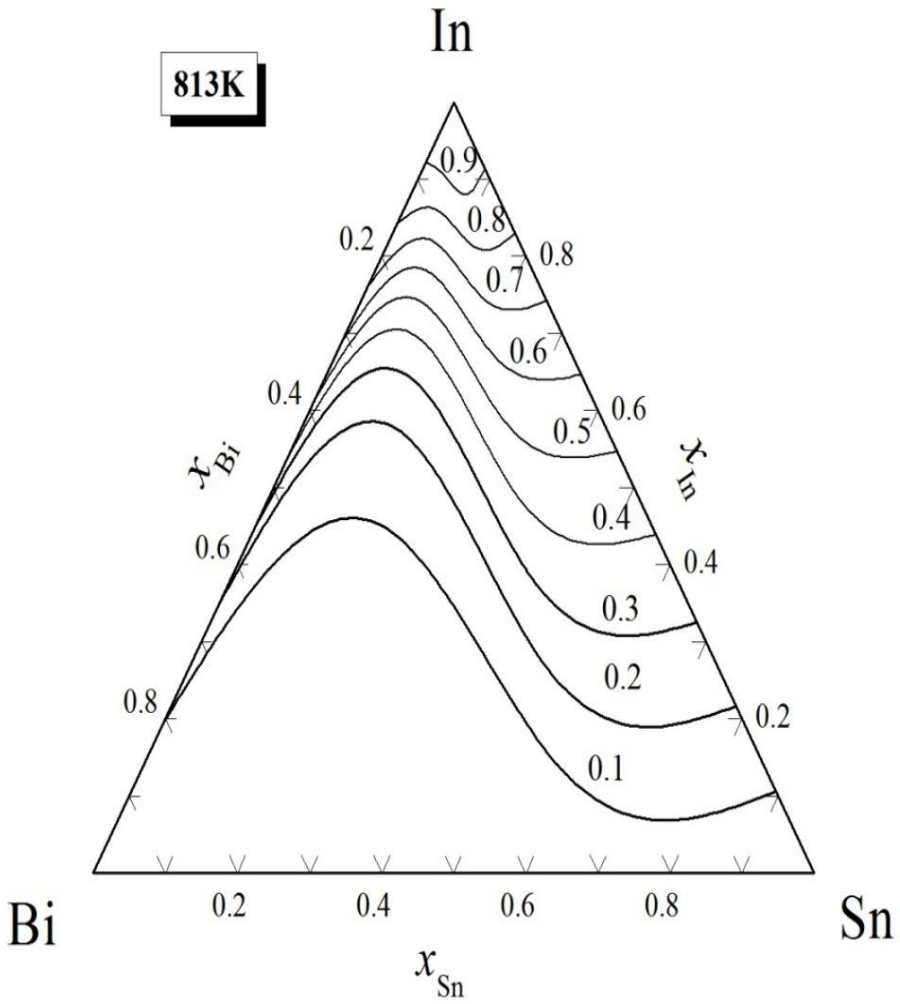

Figure 3.4 Iso-activity lines of Indium in the Bi-In-Sn liquid alloys at 813K

3.4.2 Integral molar excess free energy in In-Bi-Sn at 813K

The Darken's treatment [Darken (1950)] has been found suitable for the computation of ternary molar excess free energy from the measured activity of In over the ternary field in Bi-In-Sn system. The excess molar free energy of the solution has been obtained from equations (2.16) by graphical calculation. For the ternary excess molar free energy, it is essential to plot $\bar{G}_{In}^{xs}/ (1\text{-}x_{In})^2$ as a function of x_{In} and the integration constant ($[G_{Bi-Sn}^{xs}]_{xBi/xSn}$) is calculated from the EMF values measured at 813K and is presented in the Table 3.7. The experimental data (Table 3.4) are plotted in this manner in Figure 3.6 which show this function for Indium in each of the five ternary sections :solutions: (A) In_xBi_{1-x} (B) $In_x\text{-}(Bi_{0.67}Sn_{0.33})_{1-x}$ (C) $In_x\text{ -}(Bi_{0.50}\ Sn_{0.50})_{1-x}$ (D) $In_x\text{-}(Bi_{0.33}\ Sn_{0.67})_{1-x}$ (E) $In_x\text{-}Sn_{1-x}$.

The excess molar free energy values for the Indium –Bismuth and Indium – Tin binary systems have also been taken from literature [Vassiliev et al. (1998), Boa (1998)] by extrapolation of EMF values at 813K. The G^{xs} values obtained by equation (2.19) for five binary (pseudo-binary) systems are presented in Table 3.9, 3.10 and 3.11.The G^{xs}as a composition of In is shown in the Figure 3.7. Iso molar Gibbs free energy graph was plotted trough extracting data for G^{xs} values(i.e. -0.2, -0.9,-1.6 and -2.3 KJ) from G^{xs} vs x_{In}, G^{xs} vs x_{Bi} and G^{xs} vs x_{Sn} plots. G^{xs} vs x_{Bi} and G^{xs} vs x_{Sn} plots were obtained by following procedure:

1. Three sections at constant x_{Sn}/x_{In} = 2, 1, 0.5 were drawn from the bismuth corner of the ternary triangle along which indium composition varies.

2. These three lines intersected the experimental lines at various compositions. Those compositions were calculated with respect to indium compositions.

3. With the help of the equation (2.16), the ternary excess free energy was calculated for that composition. Similarly, the ternary excess molar free energies for the other composition were calculated along all three sections. Since, along each section, the composition of the bismuth varies, we can have the variation of ternary excess free energy as a function of bismuth composition. We can plot the G^{xs} as function of x_{Bi}.

4. The same procedure can be followed to obtain the Gxs as function of x_{Sn}. Now, we have three diagrams of G^{xs} as function of x_{Bi}, G^{xs} as function of x_{Sn} and G^{xs} as function of x_{In}. The G^{xs} data are extracted from these three diagram for the values of -0.2, -0.9,-1.6 and -2.3 KJ at 813K and plotted in the Figure 3.5.

From the Figure 3.5, it is observed that the negative values of excess free energy are predominant inside the ternary triangle i.e for most of the compositions. It could be inferred that there is strong interactions among the indium, tin and bismuth atoms in the solutions.

Table 3.7: Patial excess free energy of In-Sn-Bi system

$(Sn_{0.33}Bi_{0.67})_{1-x}$ In_x		Temperature K						
x_{In}	x_{Sn}/x_{Bi}	**723**	**745**	**767**	**789**	**813**	**833**	**855**
0.1	0.5	-6.98787	-7.07502	-7.30596	-7.46825	-7.63659	-7.89771	-8.12634
0.3		-10.19302	-10.27670	-10.55340	-10.82984	-11.10779	-11.50149	-11.80525
0.5		-10.18603	-10.30800	-10.49758	-10.89397	-11.22535	-11.57478	-11.73082
0.7		-4.17735	-4.24430	-4.31169	-4.45382	-4.60836	-4.60533	-4.86857
0.9		0.23967	0.24954	0.26371	0.27826	0.29392	0.30852	0.31138

$(Sn_{0.50}Bi_{0.50})_{1-x}$ In_x		Temperature(K)						
x_{In}	x_{Sn}/x_{Bi}	**723**	**745**	**767**	**789**	**813**	**833**	**855**
0.1	1	-10.04630	-10.03100	-10.20915	-10.48249	-10.58112	-10.74271	-11.06341
0.3		-6.0097	-6.07965	-6.21728	-6.31610	-6.36459	-6.34582	-6.45449
0.5		-1.57700	-1.62338	-1.61948	-1.57957	-1.61044	-1.56273	-1.51547
0.7		-0.02807	-0.00050	0.00904	0.00930	0.02886	0.02957	0.07213
0.9		0.34412	0.35436	0.36483	0.37529	0.38671	0.38895	0.40561

$(Sn_{0.67}Bi_{0.33})_{1-x}$ In_x		Temperature (K)						
x_{In}	x_{Sn}/x_{Bi}	**723**	**745**	**767**	**789**	**813**	**833**	**855**
0.1	2	-2.37328	-2.27415	-2.11610	-2.15125	-2.18113	-2.02846	-1.96768
0.3		-2.53513	-2.49719	-2.54588	-2.52734	-2.44319	-2.35508	-2.26971
0.5		-1.39718	-1.36111	-1.39257	-1.43104	-1.45812	-1.51085	-1.56846
0.7		-0.79963	-0.79411	-0.84633	-0.83721	-0.86406	-0.89658	-0.92026
0.9		0.31408	0.32181	0.33065	0.34082	0.35118	0.35982	0.36737

Table 3.8 Free energy function of Indium for Bi-In-Sn alloys at 813K

$(Sn_{0.33}Bi_{0.67})_{1-x}$ In_x	x_{Sn}/x_{Bi} = 0.5	$G^{XS}_{In}/(1-x_{In})^2$(KJ)
x_{In}		-9.420882978
0.1		-22.72397703
0.3		-44.78255101
0.5		-51.18715728
0.7		29.0451615
0.9		-9.420882978
$(Sn_{0.50}Bi_{0.50})_{1-x}$ In_x		
0.1	x_{Sn}/x_{Bi} = 1	-13.06787297
0.3		-13.05031818
0.5		-6.448952364
0.7		0.277494152
0.9		38.4866251
$(Sn_{0.67}Bi_{0.33})_{1-x}$ In_x		
0.1	x_{Sn}/x_{Bi} = 2	-2.696137445
0.3		-4.99655077
0.5		-5.836899177
0.7		-9.569344507
0.9		37.12887009

Table 3.9 Integral excess molar thermodynamic quantities of Bi-In-Sn alloys at 813K along constant isoplathes.

x_{In}	G^{XS}		
	x_{Sn}/x_{Bi} = 0.5	x_{Sn}/x_{Bi} = 1	x_{Sn}/x_{Bi} = 2
0	0.277307	0.343664	0.339705
0.1	-0.57992	-0.86721	0.114467
0.3	-2.52457	-2.6724	-0.57599
0.5	-5.15882	-2.87239	-0.88705
0.7	-6.201	-1.96396	-1.07722
0.9	-2.50167	-0.35349	-0.22398
1	0	0	0

Table 3.10 Integral excess molar thermodynamic quantities of Bi-In at 813K

x_{In}	0.050	0.100	0.200	0.300	0.400	0.500	0.600	0.625	0.667	0.700	0.800	0.900
G^{XS}	-0.241	-0.508	-0.947	-1.41	-1.815	-1.879	-1.885	-2.009	-1.829	-1.73	-1.36	-0.84

Table 3.11 Integral excess molar thermodynamic quantities of Bi-Sn at 813K

x_{Bi}	0.896	0.758	0.705	0.598	0.501	0.405	0.297	0.199	0.105
G^{XS}	0.0009	0.0008	0.0007	0.0006	0.0005	0.0004	0.0003	0.0002	0.00011

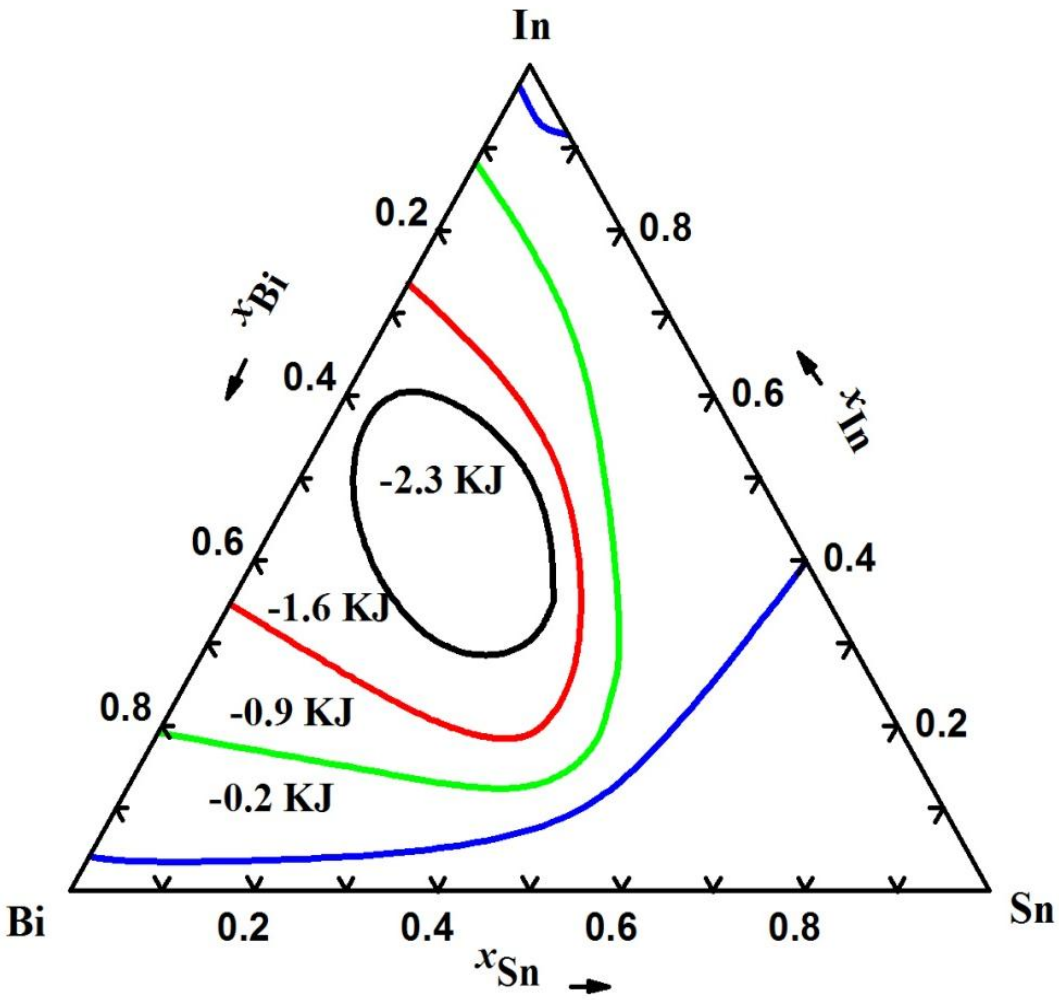

Figure 3.5 Iso Gibbs free energy curve Bi-In-Sn ternary alloy

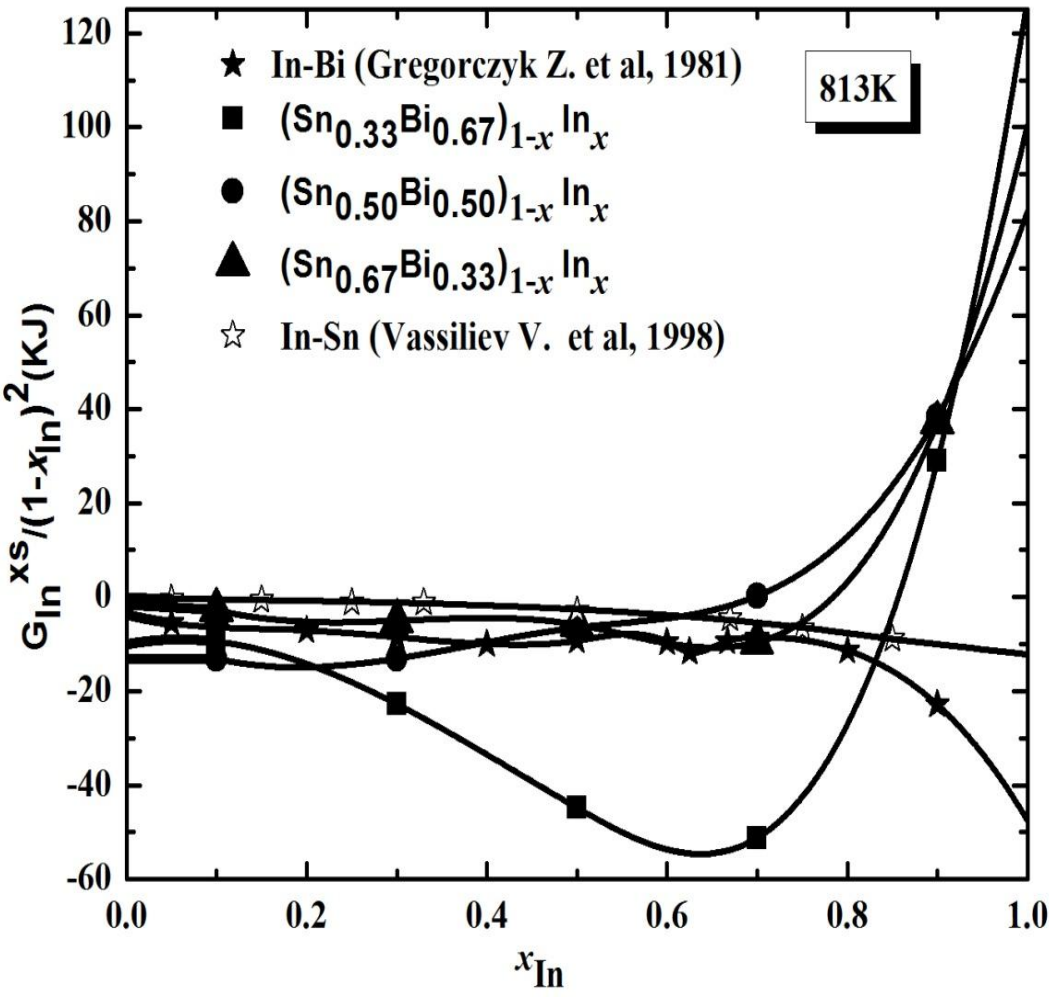

Figure 3.6 Free energy function of In in Bi-In-Sn alloys at 813K

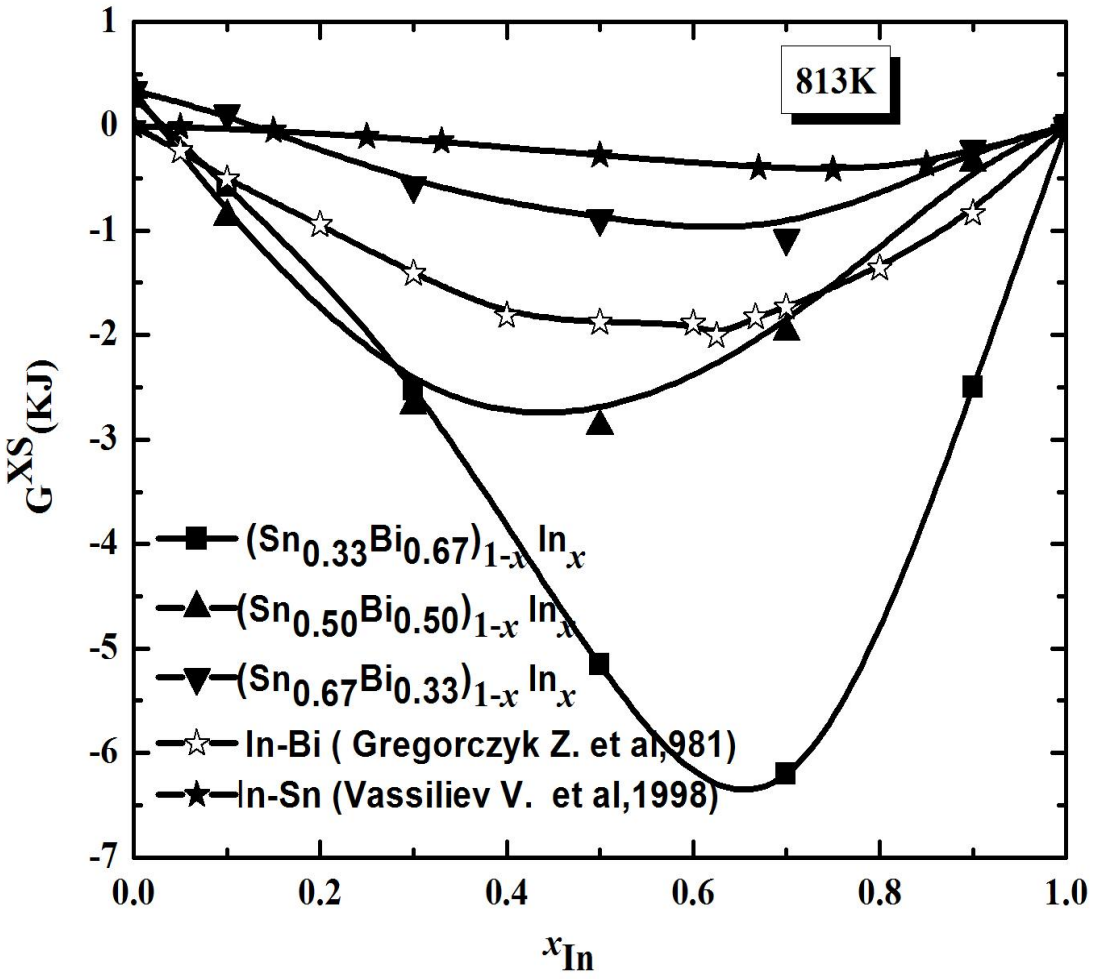

Figure 3.7 G^{xs} as a function of x_{In} at 813K

Gibbs free energy model [Moelans et al. (2003), Malakhov et al (2000) Muggianu et al. (1975), Boa and Ansara (1998) and Liu et al. (2001)].

In this model, the excess molar free energy of ternary solution has been calculated by using binary interaction parameters and ternary interaction parameters. The excess Gibbs free energy for the present system has been calculated by using equation (2.18) and its used form for current system is given below.

$$G^{XS} = x_{Bi}x_{In}\left(0_{L_{Bi,In}} + (x_{Bi} - x_{In})1_{L_{Bi,In}} + (x_{Bi} - x_{In})^2 2_{L_{Bi,In}} + (x_{Bi} - x_{In})^3 3_{L_{Bi,In}}\right) + x_{Bi}x_{Sn}\left(0_{L_{Bi,Sn}} + (x_{Bi} - x_{Sn})1_{L_{Bi,Sn}}\right) + x_{In}x_{Sn}\left(0_{L_{In,Sn}} + (x_{In} - x_{Sn})1_{L_{In,Sn}}\right) + x_{\mathrm{In}}x_{\mathrm{Bi}}x_{\mathrm{Sn}}(\mathrm{I} \qquad 35$$

…….. (3.4)

Table 3.12 Interaction parameters for In-Bi, In-Sn and Bi-Sn binaries at 813K

Bi-In				Bi-Sn		In-Sn	
$0_{L_{Bi,In}}$	$1_{L_{Bi,In}}$	$2_{L_{Bi,In}}$	$3_{L_{Bi,In}}$	$0_{L_{Bi,Sn}}$	$1_{L_{Bi,Sn}}$	$0_{L_{In,Sn}}$	$1_{L_{In,Sn}}$
-7470.20	1063.31	-128.16	620.13	1278.61	-221.055	-2087.73	-1169.02

Table 3.13 Interaction parameters for Bi-In-Sn System

L_{In}	L_{Bi}	L_{Sn}
15234	-1016	6051

After sustituting the values from Table (3.12) and Table (3.13) in Equation (3.4), molar excess Gibbs free energies for the section x_{Sn}/x_{Bi} = 2 at 813 K is obtained and these values are compared with experimental values in Figure 3.8. It is observed from the Figure that the experimental values are in good agreement with the theoretical model

values. So we could infer that the theoretical models based on the binary data may be used for the ternary thermodynamic properties.

Table 3.14 Comparison of Model values vs experimental values

x_{In}	G^{XS}(KJ)	
	Experimental values	Theoretical Values
0	0.33970	0.33970
0.1	0.11447	-0.20187
0.3	-0.57599	-0.85917
0.5	-0.88705	-1.18292
0.7	-1.07722	-1.15079
0.9	-0.22398	-0.59076
1	0	0

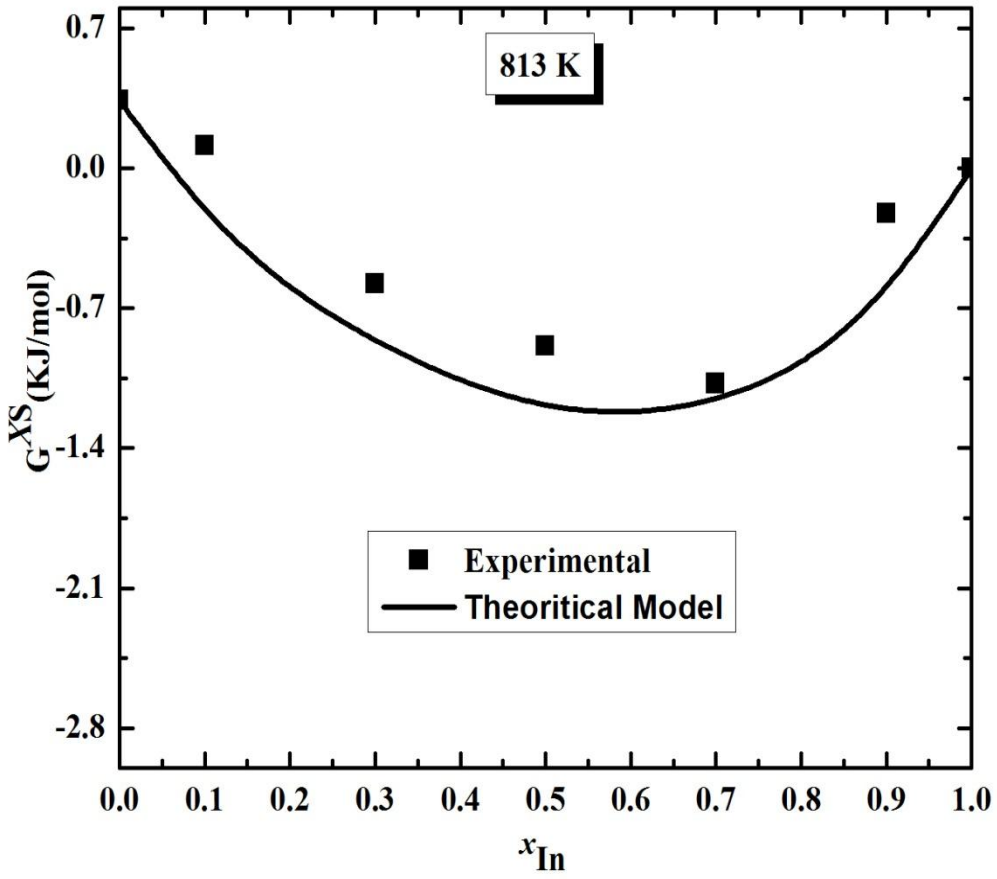

Figure 3.8 Comparison of excess molar free energy between theoretical model and this study at 813K for $(Sn_{0.67}Bi_{0.33})_{1-x}$ In_x