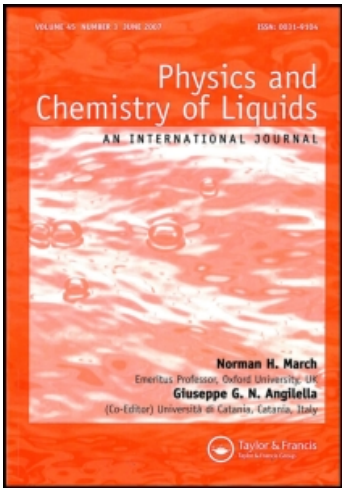

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CONCENTRATION DEPENDENT INTERACTION ENERGIES AND THERMODYNAMIC PROPERTIES OF MERCURY INDIUM LIQUID ALLOY

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The alloying behavior of mercury indium (HgIn) liquid alloy has been investigated using a model in which interaction energies are considered concentration dependent. By using the above model, the free energy of mixing, activity and long wavelength correlation functions ($S_{CC}(0)$, $S_{NN}(0)$ and $S_{NC}(0)$) have been calculated. Formation of two chemical complexes HgIn and $HgIn_6$ has been investigated in the mercury indium liquid alloy. It is concluded that chemical complex HgIn is more stable than $HgIn_6$.

KEY WORDS: Activities, concentration fluctuations.

1 INTRODUCTION

A lot of work has been done on liquid binary alloys using conformal solution model of Bhatia and coworker's[1,2,3]. Recently an interest has been renewed in the study of liquid amalgams which show anomalous behaviour in their thermodynamic properties as a function of concentration[4,5]. In this paper we reformulate the complex formation model of Bhatia and Hargrove[1] using the concentration dependent interaction energies and apply it to a specific system of mercury indium liquid alloy. In mercury indium there are maxima around the stoichiometric compositions $HgIn_6$ and HgIn followed by a deep eutectic between 0.2 and 0.45 concentration of Indium, indicating the formation of complexes HgIn and $HgIn_6$. Mercury indium alloy system melts at 258 K and in it we have a mixture of Hg atoms, In atoms, HgIn and $HgIn_6$ all in equilibrium with each other. Following Karaoglu and Young[6] we assumed the interaction energy to be a linear function of concentration.

The plan of the paper is as follows. In the second section we reformulate the conformal solution model with the assumed concentration dependent interaction energies and give expressions for G_M, ln a_A. The third section deals with the calculation of equilibrium interaction energy parameters, free energy of mixing G_M and activity a_A. The long wavelength correlation functions $S_{CC}(0)$, $S_{NN}(0)$ and $S_{NC}(0)$ are dealt within the last section. The results are compared with the conformal solution model without concentration dependent interaction energy and the experimental results. The present paper examines how best the concentration dependent interaction energy explains the thermodynamic properties of mercury indium liquid alloy particularly the stability of HgIn and $HgIn_6$ compounds.

2 CONFORMAL SOLUTION MODEL AND THE CONCENTRATION DEPENDENT INTERACTION ENERGY, EXPRESSION FOR FREE ENERGY OF MIXING AND ACTIVITY

We start with Bhatia-Hargrove model[1] and assume the formation of appropriate complexes $A_\mu B_\nu$ with μ and ν integers which are usually small. This model describes the concentration fluctuations and thermodynamics of a number of compound forming liquid alloys. For the sake of simplicity we consider that only one kind of chemical complex is formed at a time and look at the stability of each complex through G_M. We set $N = 1$ in their formulation so that the binary alloy contains in all C gm atoms of A and $(1 - C)$ gm atoms of B. In the liquid state it consists of n_1 gm atoms of A, n_2 gm atoms of B and n_3 gm moles of the complex $A_\mu B_\nu$, we have from the conservation of atoms

$$n_1 = C - \mu n_3,\ n_2 = 1 - C - \nu n_3 \tag{2.1}$$

and

$$n = n_1 + n_2 + n_3 = 1 - (\mu + \nu - 1) n_3 \tag{2.2}$$

The free energy of mixing G_M of the binary alloy may be written as

$$G_M = G - CG_1^{(0)} - (1 - C) G_2^{(0)} = - n_3 g + G' \tag{2.3}$$

with

$$g = \mu G_1^{(0)} + \nu G_2^{(0)} - G_3^{(0)} \tag{2.4}$$

and

$$G' = G - [n_1 G_1^{(0)} + n_2 G_2^{(0)} + n_3 G_3^{(0)}] \tag{2.5}$$

where g is the formation energy of the complex, and thus the term $(- n_3 g)$ in Eq. (2.3) represents the lowering of free energy due to the formation of the chemical complex $A_\mu B_\nu$. $G_i^{(0)}$, $i = 1, 2, 3$ is the chemical potential for the pure species i in the mixutre. G' represents the free energy of mixing of the ternary mixture of A, B and $A_\mu B_\nu$. Since the strong interactions are accommodated via the formation of the chemical complexes, the ternary mixture can be treated as an only weakly interacting system. Hence for G' we consider the weak interaction approximation. This enables one to express G_M as

$$G_M = - n_3 g + RT \sum_{i=1}^{3} n_i \ln(n_i/n) + \sum\sum_{i<j} \frac{n_i n_j}{n} w_{ij} \tag{2.6}$$

where

$$W_{12} = n_1 w_{11} + n_2 w_{22} \tag{2.7}$$

$w_{ij}(i,j = 1,2,3)$ are the mutual interaction energies between the three constituents of the mixture. w_{11} and w_{22} are the interaction energies in the pure liquid limits[7]. If the interaction energies between the individual species is different then the two species will interact with each other and if interaction energies of the individual species is same then there will be no interaction between the two species. The equilibrium value of n_3 at a given temperature and pressure is given by

$$\left(\frac{\partial G_M}{\partial n_3}\right)_{T,P,C} = 0 \tag{2.8}$$

Using Eqs. (2.6) and (2.8) along with Eq. (2.7), the equilibrium value of n_3 is given by

$$\frac{n_1^{\mu} n_2^{\nu}}{n_3 n^{\mu+\nu-1}} = K e^{Y} \tag{2.9}$$

where

$$K = e^{-g/RT} \tag{2.10}$$

and

$$\begin{aligned} Y = {} & \frac{w_{12}}{RT}\left((\mu+\nu-1)\frac{n_1 n_2}{n^2} - \mu\frac{n_2}{n} - \nu\frac{n_1}{n}\right) \\ & + \frac{w_{13}}{RT}\left((\mu+\nu-1)\frac{n_1 n_3}{n^2} - \mu\frac{n_3}{n} + \frac{n_1}{n}\right) \\ & + \frac{w_{23}}{RT}\left((\mu+\nu-1)\frac{n_2 n_3}{n^2} - \nu\frac{n_3}{n} + \frac{n_2}{n}\right) \\ & - \frac{1}{RT}(\mu w_{12} + \nu w_{22})\frac{n_1 n_2}{n} \end{aligned} \tag{2.11}$$

Eq. (2.9) can be solved numerically to obtain equilibrium values of n_3 via Eqs. (2.1), (2.2), and (2.11). Using Eqs. (2.1) and (2.2), Eq. (2.6) yields the equilibrium value of free energy of mixing G_M.

The activity a_A is defined as

$$RT \ln a_A = \left(\frac{\partial G_M}{\partial N_A}\right)_{T,P,N_B} = G_M + (1-C)\left(\frac{\partial G_M}{\partial C}\right)_{T,P,C} \tag{2.12}$$

Using Eqs. (2.6) and (2.7), one gets

$$RT \ln a_A = RT \ln (n_1/n) + (n_2/n)(n_1 + w_{12}) + (n_3/n)w_{13} - \frac{1}{n^2}\sum\sum_{i<j} n_i n_j w_{ij} \tag{2.13}$$

Eqs. (2.6) and (2.13) are used in the following sections to investigate the behavior of G_M and $\ln a_A$ in the molten HgIn system.

3 CALCULATION OF EQUILIBRIUM INTERACTION ENERGY PARAMETERS, FREE ENERGY OF MIXING AND ACTIVITY

The numerically calculated equilibrium values of n_3 vs c using Eq. (2.9) are shown in Figure 1 and in this case w_{12} is considered concentration dependent according to Eq. (2.7). Using these values of n_3 at different concentrations, the values of n_1, n_2 and n are calculated which can further be used to calculate numerically the best fit interaction energies w_{ij} and reaction constant g. The values of various parameters are

$$g/RT = 3.04, \quad w_{13}/RT = 1.27, \quad w_{23}/RT = 0.05,$$
$$w_{11}/RT = -0.4, \quad w_{22}/RT = -0.44 \tag{3.1}$$

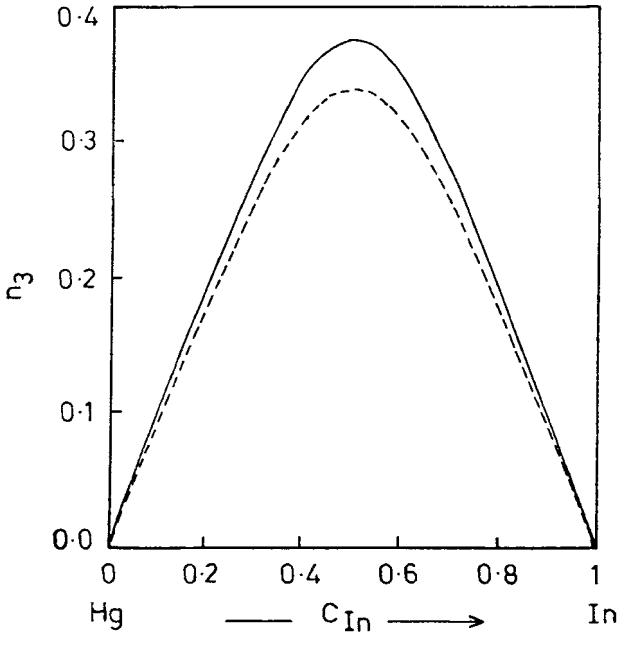

Figure 1 Chemical complex n_3 (gm mol) of HgIn (258 K) liquid alloy: (—) C dependent interaction energy, (----) without C dependent interaction energy.

Using above values of w_{11}/RT and w_{22}/RT the concentration dependent interaction energies w_{12}/RT are given in Table 1.

Using above values of interaction energy parameters and the values of n_1, n_2, n_3 and n in Eq. (2.6), the free energy of mixing G_M is calculated and is given in Figure 2 and compared with the values calculated without concentration dependent interaction energy[5]. The free energy of mixing G_M experimental[8] matches with the theoretically obtained values much better as compared to the values of G_M calculated by taking concentration independent interaction energies. The minima of G_M for both experimental and theoretical models lie at 0.5, suggesting the formation of HgIn complex and that it is the most stable phase of the liquid amalgam studied.

Table 1

C	w_{12}/RT (HgIn)	w_{12}/RT ($HgIn_6$)
0	−0.44	−0.44
.1	−0.36	−0.15
.2	−0.27	−0.13
.3	−0.19	−0.18
.4	−0.13	−0.24
.5	−0.09	−0.29
.6	−0.12	−0.34
.7	−0.18	−0.38
.8	−0.25	−0.40
.9	−0.32	−0.40
1.0	−0.40	−0.40

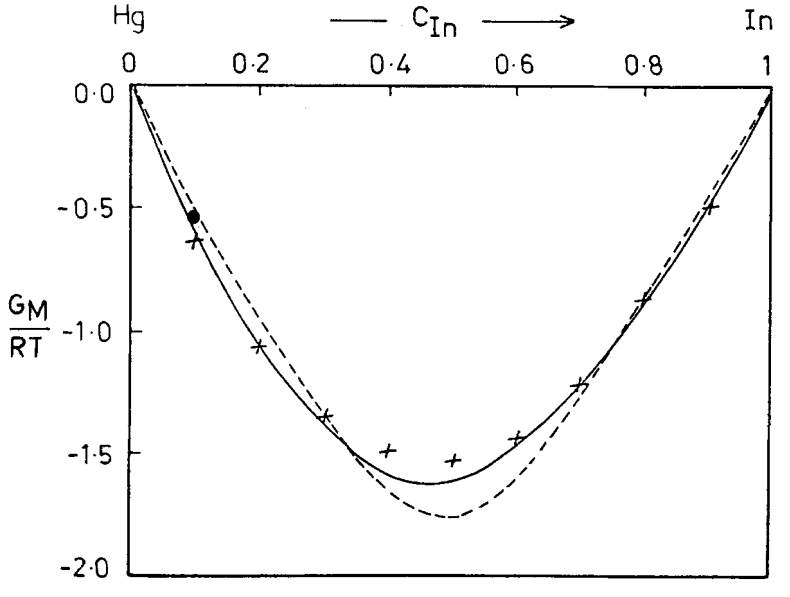

Figure 2 Free energy of mixing G_M/RT of HgIn (258 K) liquid alloy. (−) C dependent interaction energy, (----) without C dependent interaction energy, (× × ×) experiment (Hultgren *et al.* 1973).

The theoretical behavior of $\ln a_A$ vs C is plotted in Figure 3, which shows a reasonable agreement with the experimental values[8]. The theoretical behavior of $\ln a_A$ vs C in which w_{12} is considered concentration independent is also plotted in Figure 3.

4 LONG WAVELENGTH CORRELATION FUNCTIONS

The long wavelength correlation functions given by Bhatia and Thornton[2] corresponding to the fluctuations in concentration-concentration correlation functions, $S_{CC}(0)$, number-number correlation functions $S_{NN}(0)$ and the number concentration correlation functions $S_{NC}(0)$ have been widely used to understand the stability[3,9,10] of the binary mixtures. The correlation functions are related with the thermodynamic functions,

$$S_{CC}(0) = RT\left(\frac{\partial^2 G_M}{\partial C^2}\right)^{-1}_{T,P,N} = (1-C)\,a_A\left(\frac{\partial a_A}{\partial C}\right)^{-1}_{T,P,N} \tag{4.1}$$

$$S_{NN}(0) = \rho\, k_B T \kappa_T + \delta^2 S_{CC}(0) \tag{4.2}$$

$$S_{NC}(0) = -\delta S_{CC}(0) \tag{4.3}$$

and

$$\delta = (V_1 - V_2)/(CV_1 + (1-C)V_2) \tag{4.4}$$

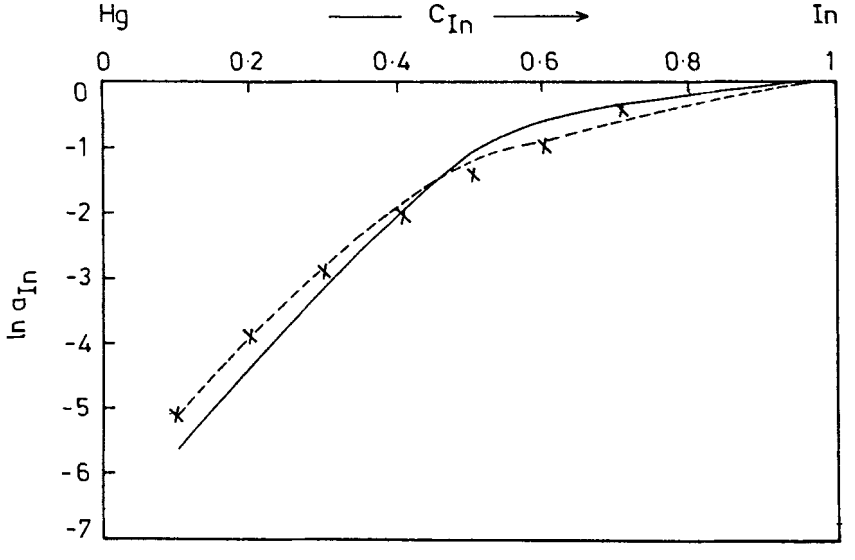

Figure 3 Activity ($\ln a_{In}$) of In in HgIn (258 K) liquid alloy. Curves and points have the same meaning as in Figure 2.

where V_1 and V_2 are the partial molar volumes per atoms of the two species, ρ is the number density, κ_T is the isothermal compressibility and δ stands for dilatation factor.

The most important quantity $S_{CC}(0)$ in the long wavelength limit is obtained by differentiating Eq. (2.6) with respect to C and using Eqs. (2.1) and (2.2) i.e.

$$S_{CC}(0) = \left[\sum_{i=1}^{3} \frac{(n_i')^2}{n_i} - \frac{(n')^2}{n} + \frac{2n}{RT} \sum\sum_{i<j} \left(\frac{n_i}{n}\right)' \left(\frac{n_j}{n}\right)' w_{ij} + \frac{2}{RT} \left(\frac{n_1 n_2}{n}\right)' [n_1' w_{11} + n_2' w_{22}] \right]^{-1} \tag{4.5}$$

This equation gives the theoretical behavior of $S_{CC}(0)$ for HgIn system and is given in Figure 4, which is compared with the experimental values obtained directly from activity data[8] using last two identities of Eq. (4.1). Plot of $S_{CC}(0)$ vs C, Figure 4 shows that (i) the system has a tendency to form chemical complexes that is reflected in terms of reaction constant g/RT which is >0 (ii) as $S_{CC}(0)$ is a response function, stability requires it to be + ve, but simultaneously the deviation of $S_{CC}(0)$ from ideal values ($S_{CC}^{id(0)} = C(1-C)$) is maximum at the compound forming concentration in which the interaction energy is concentration dependent as compared to the behavior of $S_{CC}(0)$ in which interaction energy w_{12} is considered as concentration independent. Equation (4.5) have been used to obtain $S_{NN}(0)$ and $S_{NC}(0)$ as a function of concentration. Because of lack of experimental data on κ_T with C, for the binary alloy HgIn a linear variation of isothermal compressibility with

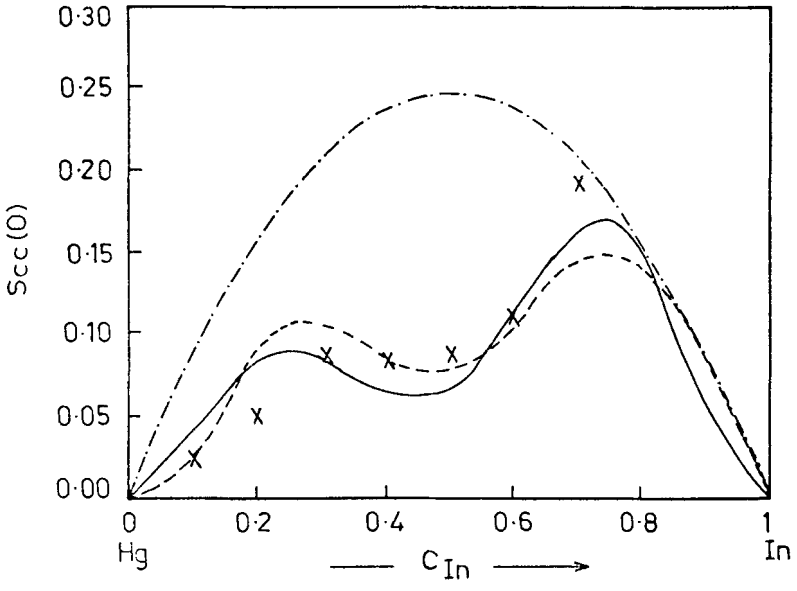

Figure 4 Concentration fluctuation ($S_{CC}(0)$) of HgIn (258 K) liquid alloy. Solid curve and the dashed curve have the same meaning as in Figure 2, ($\times \times \times$) computed directly from activity data (Hultgren *et al.* 1973), ($- \cdot - \cdot -$) corresponds to ideal values (i.e., $C(1-C)$).

concentration C is used as

$$\kappa_T = C^{\text{In}}\kappa_T + (1-C)^{\text{Hg}}\kappa_T \tag{4.6}$$

corresponding to known isothermal compressibility of pure metals. The computed values of $S_{NN}(0)$ and $S_{NC}(0)$ for HgIn are given in Figure 5 and Figure 6 respectively

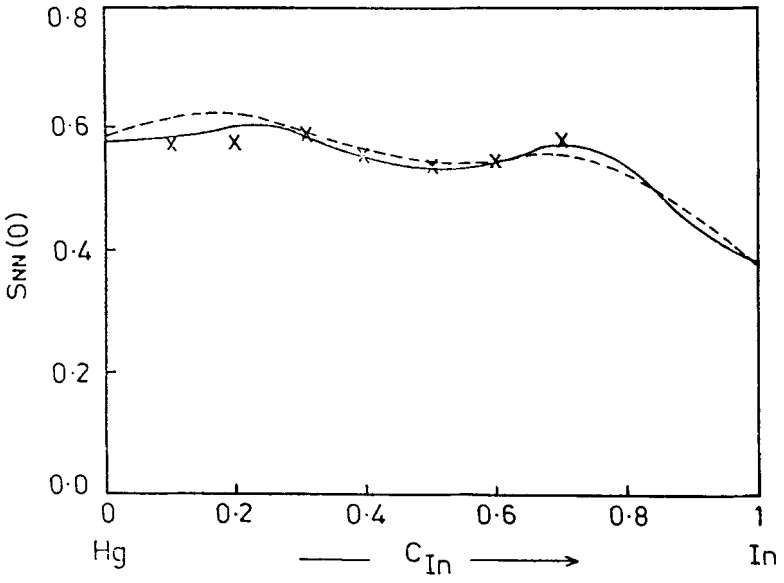

Figure 5 Number-number correlation function ($S_{NN}(0)$) of HgIn (258 K) liquid alloy. Curves and points have the same meaning as in Figure 2.

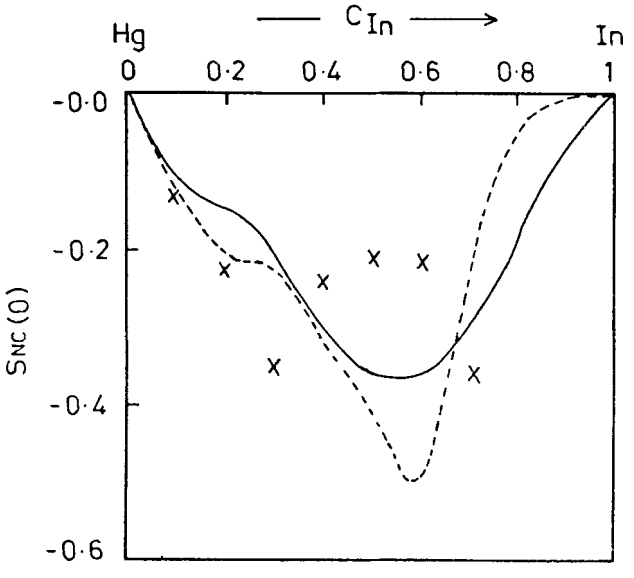

Figure 6 Number concentration correlation function ($S_{NC}(0)$) of HgIn (258 K) liquid alloy. Curves and points have the same meaning as in Figure 2.

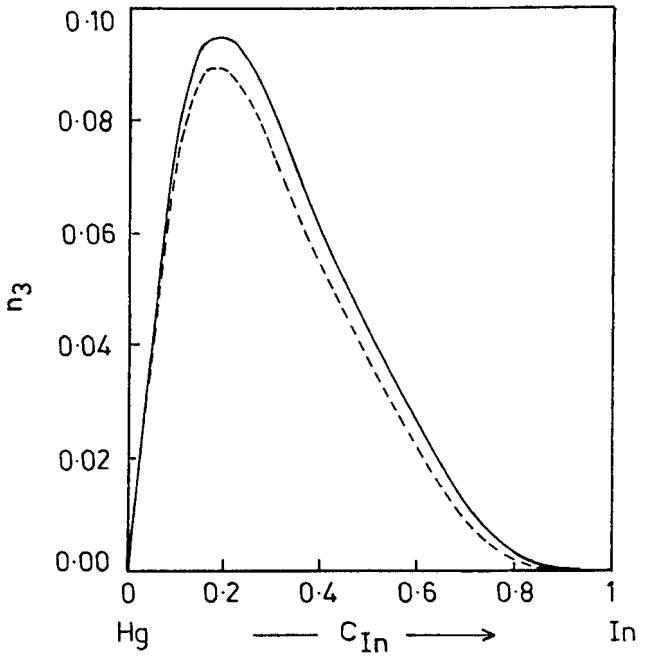

Figure 7 Chemical complex n_3 (gm mol) of $HgIn_6$ (258 K) liquid alloy. Solid curve and dashed curve have the same meaning as in Figure 1.

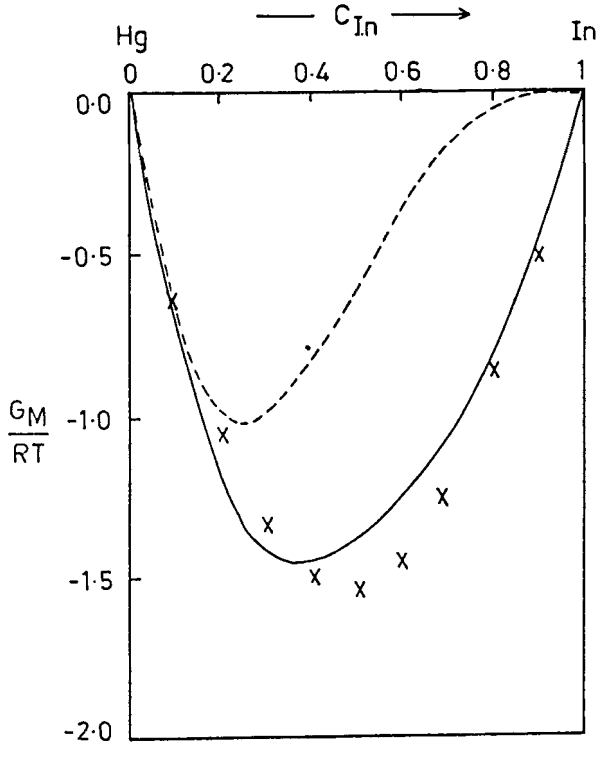

Figure 8 Free energy of mixing G_M/RT of $HgIn_6$ (258 K) liquid alloy. Curves and points have the same meaning as in Figure 2.

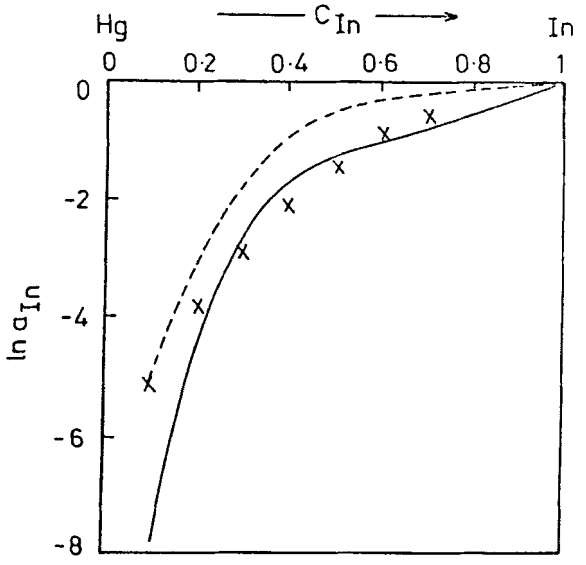

Figure 9 Activity (ln a_{In}) of In in $HgIn_6$ (258 K) liquid alloy. Curves and points have the same meaning as in Figure 2.

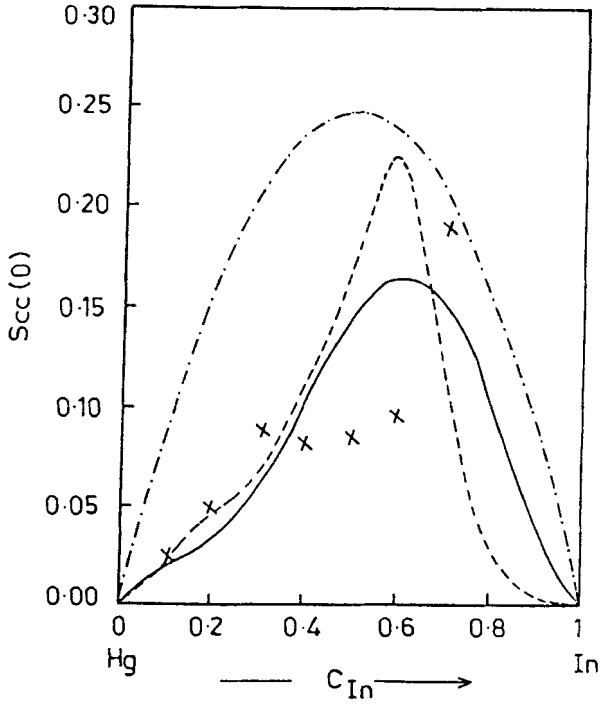

Figure 10 Concentration fluctuation ($S_{cc}(0)$) of $HgIn_6$ (258 K) liquid alloy. Curves and points have the same meaning as in Figure 4.

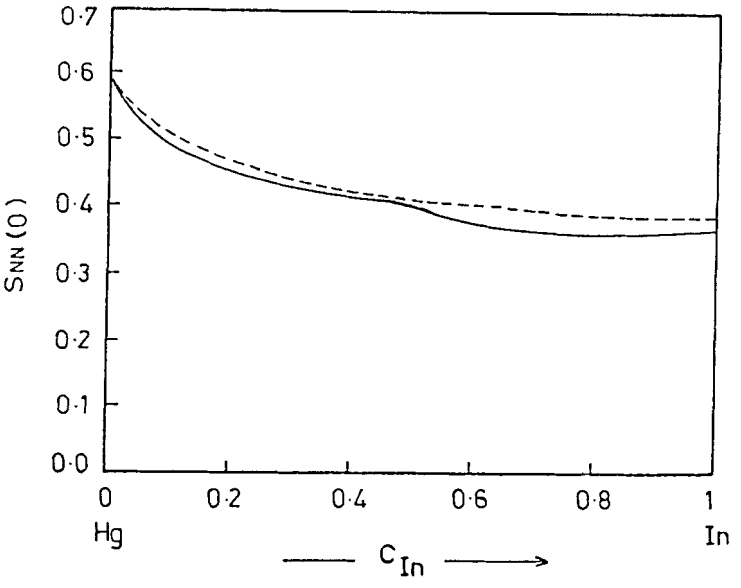

Figure 11 Number-number correlation function ($S_{NN}(0)$) of $HgIn_6$ (258 K) liquid alloy. Solid and dashed curve have the same meaning as in Figure 2.

which are compared to those obtained directly from activity data and values calculated by taking interaction energy w_{12} concentration independent. Figure 5 and Figure 6 shows that there is an improvement of $S_{NN}(0)$ and $S_{NC}(0)$ by taking concentration dependent interaction energies. Graphs of n_3, G_M, acitivity, $S_{CC}(0)$, $S_{NN}(0)$ and

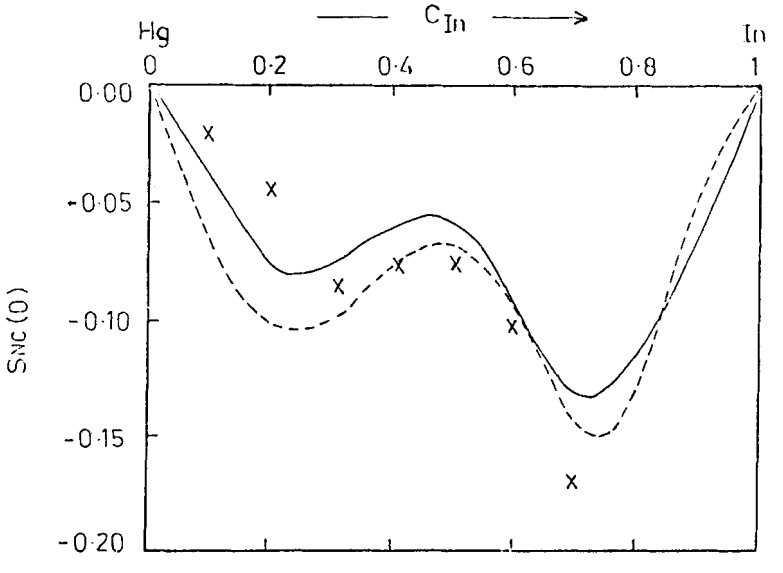

Figure 12 Number concentration correlation function ($S_{NC}(0)$) of $HgIn_6$ (258 K) liquid alloy. Curves and points have the same meaning as in Figure 4.

$S_{NC}(0)$ for $HgIn_6$ are given in Figures from 7 to 12. Though there is an improvement of G_M and activity with the experimental data[8] but the deviation in experimental and theoretical results for $S_{CC}(0)$, $S_{NN}(0)$ and $S_{NC}(0)$ confirms that $HgIn_6$ complex is not stable.

5 CONCLUSIONS

In this paper we have studied the thermodynamic properties and the long wavelength correlation functions of mercury indium molten alloy and have investigated the formation of HgIn and there is a better matching of the concentration dependent $S_{CC}(0)$ with the experimental results. The plot for $S_{CC}(0)$ corresponding to $HgIn_6$ once again confirms that it is not a stable complex. Still we have considered the formation of one complex at a time. The possibility of both complexes coexisting cannot be ruled out and is being studied further.

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