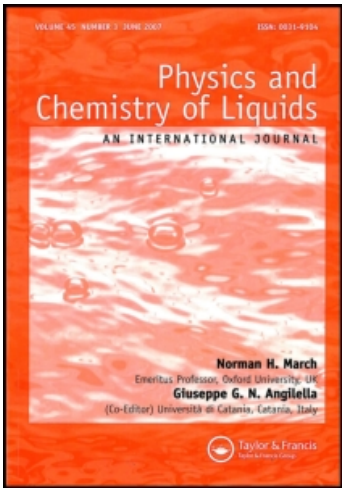

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Concentration Fluctuations and Thermodynamics of Compound Formation in Mercury Indium Liquid Alloy

K. S. Attri[a]; P. K. Ahluwalia[a]; K. C. Sharma[a]
[a] Physics Department, H.P. University, Shimla

To cite this Article Attri, K. S. , Ahluwalia, P. K. and Sharma, K. C.(1994) 'Concentration Fluctuations and Thermodynamics of Compound Formation in Mercury Indium Liquid Alloy', Physics and Chemistry of Liquids, 26: 4, 225 — 235
To link to this Article: DOI: 10.1080/00319109408029495
URL: http://dx.doi.org/10.1080/00319109408029495

Phys. Chem. Liq., 1994, Vol. 26, pp. 225–235
Reprints available directly from the publisher
Photocopying permitted by license only

CONCENTRATION FLUCTUATIONS AND THERMODYNAMICS OF COMPOUND FORMATION IN MERCURY INDIUM LIQUID ALLOY

K. S. ATTRI, P. K. AHLUWALIA AND K. C. SHARMA

Physics Department, H.P. University, Shimla-171 005.

(Received 3 March 1993)

The alloying behavior of a mercury indium (HgIn) liquid alloy has been investigated using a model which assumes that, if in solid state, compounds are formed at one or more stoichiometric compositions, then there is a possibility of the existence of these chemical complexes near the melting point as well. For this purpose the free energy of mixing, activity and long wavelength correlation functions viz. $S_{CC}(0)$, $S_{NN}(0)$ and $S_{NC}(o)$ have ben calculated and discussed in the above model. Formation of the two chemical complexes HgIn and $HgIn_6$ has been investigated in the mercury indium liquid alloy. The work confirms that HgIn is a stable complex compared to $HgIn_6$.

KEY WORDS: Liquid amalgams, chemical complexes, activity.

1 INTRODUCTION

Recently there has been a lot of interest in liquid amalgams. Jha *et al.*[1] have demonstrated in particular that their thermodynamic properties show anomalous behavior as a function of concentration. For example, 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 In, indicating the formation of complexes HgIn and $HgIn_6$. The Gibbs free energy and enthalpy is symmetrical[2] around the equiatomic concentration i.e. $C = 1/2$. The present paper examines these aspects; in particular the question of which of these two complex formations is more stable, assuming the existence of any one complex formation at a time.

Faber[3] was the first to look at the compound formation in liquid alloys. Assuming that if compounds are formed at one or more stoichiometric compositions in solid state, these are very likely to exist in the liquid state at these compositions. In the light of this we have studied thermodynamic properties viz. free energy of mixing, activity and correlation functions in the long wavelength limit of the binary molten HgIn alloy. HgIn alloy system melts at 258 K and in it signatures of two chemical complexes HgIn and $HgIn_6$ are found i.e. the molten alloy consists of a mixture of Hg atoms, In atoms and chemical complex HgIn and $HgIn_6$, all in equilibrium with each other.

Compound forming model has been used with a reasonable success in the case of alkali amalgams as shown by Jha *et al.*[1]. In this paper we investigate the HgIn liquid alloy system using compound forming model. Plan of the paper is as follows. In the second section we briefly outline the conformal solution model and give expressions for G_M, $\ln a_A$, $S_{CC}(0)$, $S_{NN}(0)$ and $S_{NC}(0)$ in the long wavelength limit. The third section deals with the calculation of interaction parameters, free energy of mixing G_M and activity a_A (A = Hg or In). The long wavelength correlation funcations ($S_{CC}(0)$, $S_{NN}(0)$ and $S_{NC}(0)$) are dealt within the last section.

2 CONFORMAL SOLUTION MODEL AND EXPRESSIONS FOR G_M AND a_A

We use here the model given by Bhatia and Hargrove[4] and assume the formation of appropriate complexes $A_\mu B_\nu$, with μ and ν integers which are usually small. This model has been used to describe concentration fluctuations and thermodynamic properties of a number of compound forming liquid alloy systems. We consider here for simplicity that one type of chemical complex is formed at a time and look at the stability of each complex through G_M. The advantage of the present approach is that it describes the concentration dependence of the thermodynamic properties quantitatively and one may infer the number of chemical complexes existing at any given temperature and pressure. Following the formulation of Bhatia and Hargrove (1974) but setting their $N = 1$, the binary alloy is allowed to contain 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:

$$n_1 = C - \mu n_3; \quad n_2 = (1 - C) - \nu n_3 \tag{2.1}$$

and

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

The equilibrium value of n_3 at a given temperature and pressure is determined by the condition

$$\left(\frac{\partial G_M}{\partial n_3}\right)_{T,P,C} = 0 \tag{2.3}$$

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

$$G_M = G - CG_1^{(0)} - (1 - C)G_2^{(0)} = -n_3 g + G' \tag{2.4}$$

with

$$g = \mu G_1^{(0)} + \nu G_2^{(0)} - G_3^{(0)} \tag{2.5}$$

and

$$G' = G - [n_1 G_1^{(0)} + n_2 G_2^{(0)} + n_3 G_3^{(0)}] \tag{2.6}$$

Where $G_i^{(0)}$, $i = 1, 2, 3$ is the chemical potential for the pure species i in the mixture. In Eq. (2.4), the first term $(-n_3 g)$ represents the lowering of free energy due to the formation of chemical complexes $A_\mu B_\nu$, while G represents the free energy of mixing of the ternary mixture of A, B and $A_\mu B_\nu$. These constituents interact weakly with one another since the strong interactions are accommodated via the formation of the chemical complexes. Thus G' is determined in the weak interaction approximation. This enables one to write G_M as

$$G_M = -n_3 g + \mathrm{RT} \sum_{i=1}^{3} n_i \ln\left(\frac{n_i}{n}\right) + \sum\sum_{i<j} \frac{n_i n_j}{n} w_{ij} \tag{2.7}$$

where w_{ij} $(i, j = 1, 2, 3)$ are the mutual interaction energies between the three constituents of the mixture. Using Eq. (2.3) and Eq. (2.7) the equilibrium value of n_3 is given by

$$\frac{n_1^\mu n_2^\nu}{n_3 n^{\mu+\nu-1}} = K e^Y \tag{2.8}$$

where

$$K = e^{-g/\mathrm{RT}} \tag{2.9}$$

and

$$\begin{aligned} Y = &\frac{w_{12}}{\mathrm{RT}}\left((\mu+\nu-1)\frac{n_1 n_2}{n^2} - \mu\frac{n_2}{n} - \nu\frac{n_1}{n}\right) \\ &+ \frac{w_{13}}{\mathrm{RT}}\left((\mu+\nu-1)\frac{n_1 n_3}{n^2} - \mu\frac{n_3}{n} + \frac{n_1}{n}\right) \\ &+ \frac{w_{23}}{\mathrm{RT}}\left((\mu+\nu-1)\frac{n_2 n_3}{n^2} - \nu\frac{n_3}{n} + \frac{n_2}{n}\right) \end{aligned} \tag{2.10}$$

On eliminating n_1, n_2 and n in Eqs. (2.8) and (2.10) via Eqs. (2.1) and (2.2), the Eq. (2.8) is seen to be an expression in single unknown variable n_3, which may be obtained as the root of Eq. (2.8). Using (2.1), (2.2) and (2.7) yields the equilibrium free energy of mixing G_M.

The activity a_A is defined as

$$\mathrm{RT}\ \ln a_A = \left(\frac{\partial G_M}{\partial N_A}\right)_{T,P,N_B} = G_M + (1 - C)\left(\frac{\partial G_M}{\partial C}\right)_{T,P,C} \tag{2.11}$$

Using Eq. (2.7), one gets

$$\mathrm{RT} \ln a_A = \mathrm{RT}\ \ln\left(\frac{n_1}{n}\right) + \left(\frac{n_2}{n}\right) w_{12} + \left(\frac{n_3}{n}\right) w_{13} - \frac{1}{n^2} \sum\sum_{i<j} n_i n_j w_{ij} \tag{2.12}$$

These two Eqs. (2.7) and (2.12) are used in the following sections to investigate the behavior of G_M and $\ln a_A$ in the molten HgIn system.

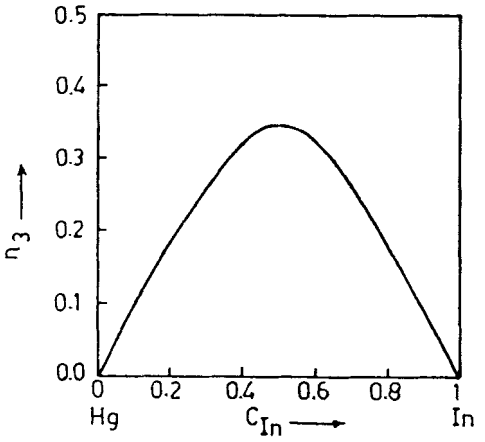

Figure 1 Chemical complex n_3 (gm mol) of HgIn (258 K) liquid alloy.

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

In order to investigate the specific system first we solve Eq. (2.8) numerically to obtain the equilibrium value of n_3 for various concentrations as given in Figure 1. 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 the parameters are

$$\frac{g}{RT} = 5.64, \quad \frac{w_{12}}{RT} = -0.4, \quad \frac{w_{13}}{RT} = 1.25, \quad \frac{w_{23}}{RT} = 0.72 \tag{3.1}$$

Using these values of interaction parameters and the values of n_1, n_2, n_3 and n in Eq. (2.7), the free energy of mixing G_M was calculated given in Figure 2. The free

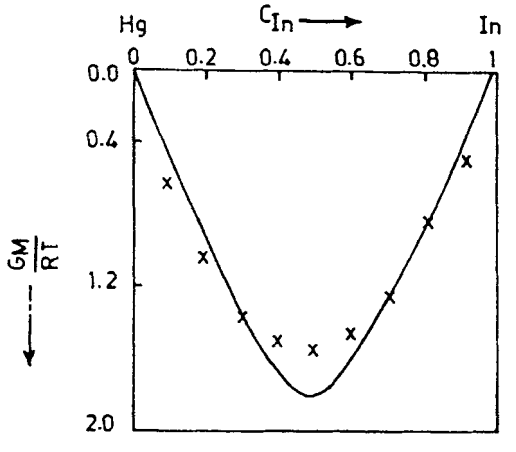

Figure 2 Free energy of mixing GM/RT of HgIn (258 K) liquid alloy. (—) theory, ($\times$ $\times$ $\times$) experiment (Hultgren *et al.*, 1973).

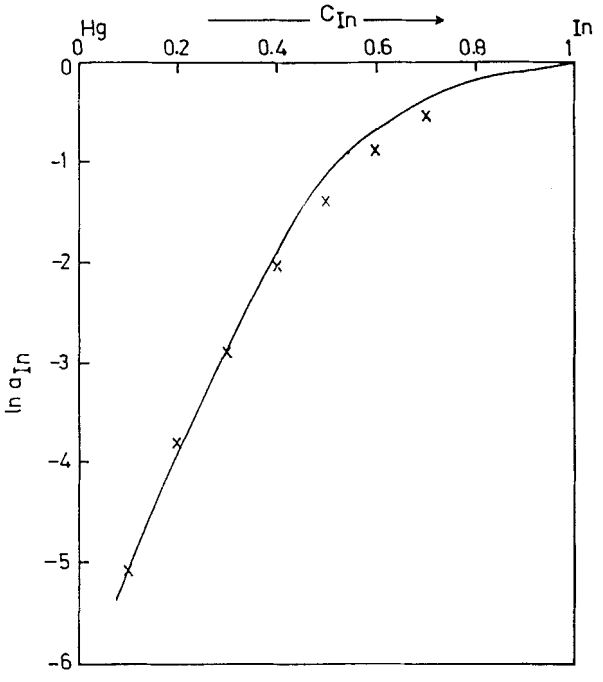

Figure 3 Activity (ln a_{In}) of In in HgIn (258 K) liquid alloy, (—), theory and (× × ×), experiment (Hultgren *et al.*, 1973).

energy of mixing G_M experimental (Hultgren *et al.*, 1973) matches with the theoretically obtained values. The minima of G_M for both experimental and theoretical models used lies at 0.5, suggesting the formation of HgIn complex and that it is the most stable phase of the liquid amalgam.

The theoretical behavior of ln a_A vs C, Figure 3, is found to exhibit a reasonable agreement between the experimental (Hultgren *et al.*, 1973) values.

4 LONG WAVELENGTH CORRELATION FUNCTIONS

Since the work by Bhatia and Thornton[5], the long wavelength limit of three correlation functions 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[6–8] of the binary mixtures. These correlation functions are

related with the thermodynamic functions,

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

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

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

and

$$\delta = (V_1 - V_2)/(CV_1 + (1-C)V_2)$$

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, concentration-concentration fluctuations $S_{CC}(0)$ in the long wavelength limit is obtained by differentiating Eq. (2.7) with respect to C and using Eqs. (2.1), (2.2) and (2.8) i.e.

$$S_{CC}(0) = \left[\sum_{i=1}^{3}\frac{(n_i')^2}{n_i} - \frac{(n')^2}{n} + \frac{2n}{\mathrm{RT}}\sum\sum_{i<j}\left(\frac{n_i}{n}\right)'\left(\frac{n_j}{n}\right)' w_{ij}\right]^{-1} \tag{4.4}$$

This equation gives the theoretical behavior of $S_{CC}(0)$. The theoretical behavior of $S_{CC}(0)$ for HgIn is given in Figure 4 which is compared with the experimental values obtained directly from the activity data[2] using the last two identities of

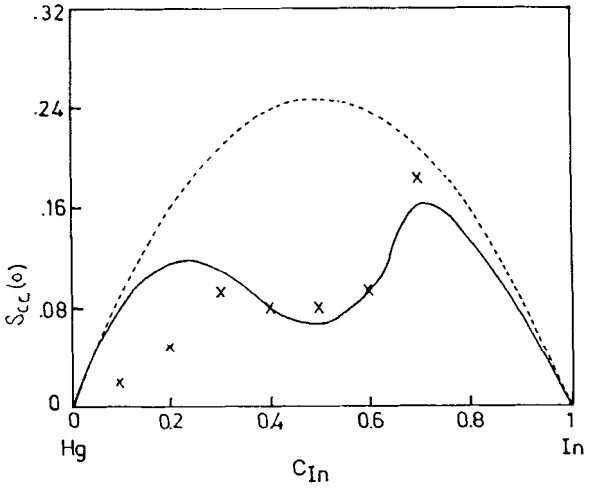

Figure 4 Concentration fluctuation ($S_{cc}(0)$) of HgIn (258 K) liquid alloy, (—) theory, (× × ×) computed directly from activity data[2], (- - -) corresponds to ideal values (i.e. $C(1-c)$).

Eq. (4.1). Plot of $S_{CC}(0)$ vs C shows that (i) the system has a tendency to form chemical complexes that is reflected in terms of values of reaction constant g/RT which is >0, and the values of interaction energies w_{12}, w_{13} and w_{23}. (ii) the deviation of $S_{CC}(0)$ from the ideal values ($S^{id}_{CC}(0) = C(1 - C)$) is maximum at the compound forming concentration. $S_{CC}(0)$ apart from being zero at $C = 0$ and $C = 1$, is minimum at $C = C_c$ and has two peaks, one between $0 < C < C_c$ and other between $C_c < C < 1$, depending on the values of μ, ν and g. For $C > C_c$ the ternary mixture of atoms A, B and complex $A_\mu B_\nu$ can be thought as a binary mixture of B atoms and complex $A_\mu B_\nu$ for $C < C_c$ and of A atoms and complex $A_\mu B_\nu$ for $C < C_c$. The $S_{CC}(0)$ as computed from Eq. (4.4) 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 concentration C is used as

$$\kappa_T = C\,{}^{In}\kappa_T + (1 - C)\,{}^{Hg}\kappa_T \tag{4.5}$$

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 which are compared with those obtained directly from activity data. The dip in $S_{NN}(0)$ and $S_{NC}(0)$ is clearly visible for HgIn composition corresponding to $\mu = 1$, $\nu = 1$. Graphs of n_3, G_M, activity, $S_{CC}(0)$, $S_{NC}(0)$, $S_{NN}(0)$ Figure 7 to 12 confirm that $HgIn_6$ complex is not stable.

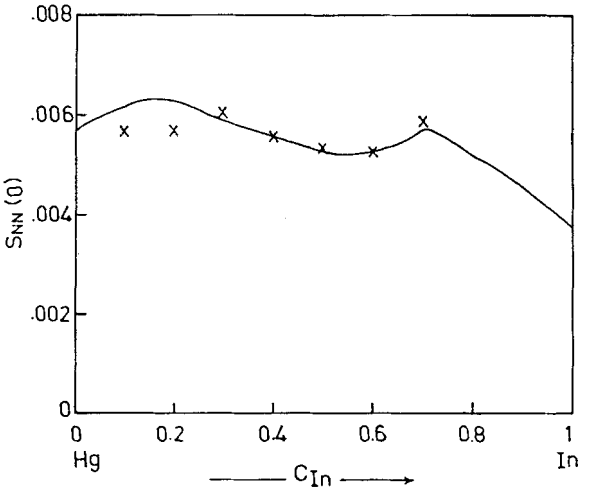

Figure 5 Number-number correlation function of HgIn (258 K) liquid alloy. Curve and points have the same meaning as in Figure 4.

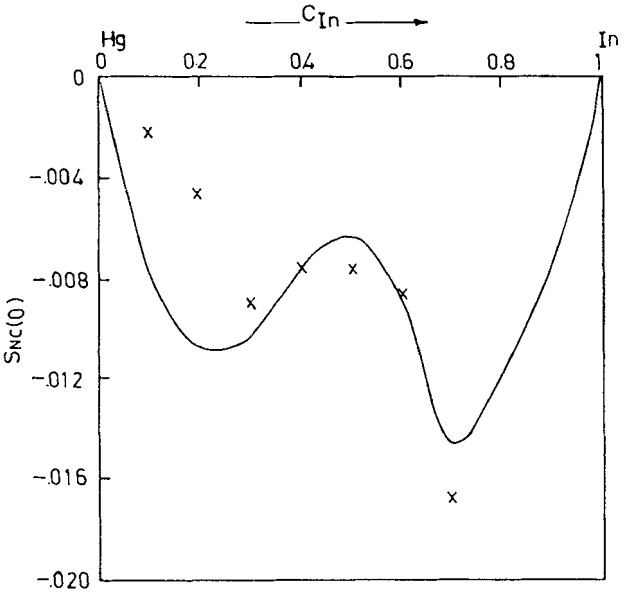

Figure 6 Number concentration correlation function of HgIn (258 K) liquid alloy. Curve and points have the same meaning as in Figure 4.

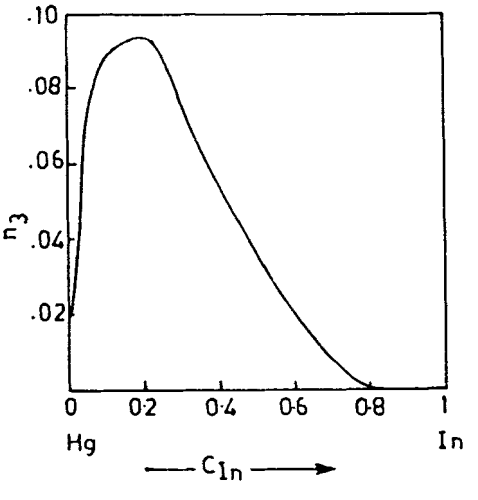

Figure 7 Chemical complex n_3 (gm mol) of $HgIn_6$ (258 K) liquid alloy.

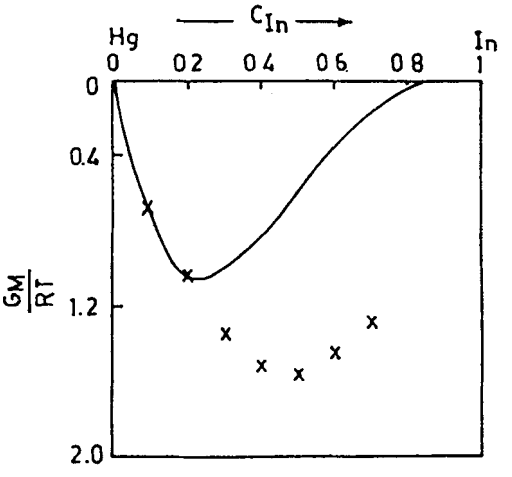

Figure 8 Free energy of mixing G_M/RT *of* $HgIn_6$ (258 K) liquid alloy. Curve and points have the same meaning as in Figure 2.

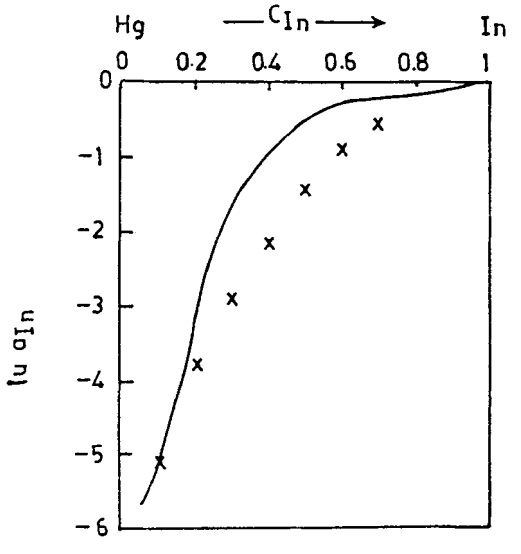

Figure 9 Activity ($\ln a_{In}$) of In in $HgIn_6$ (258 K) liquid alloy. Curve and points have same meaning as in Figure 3.

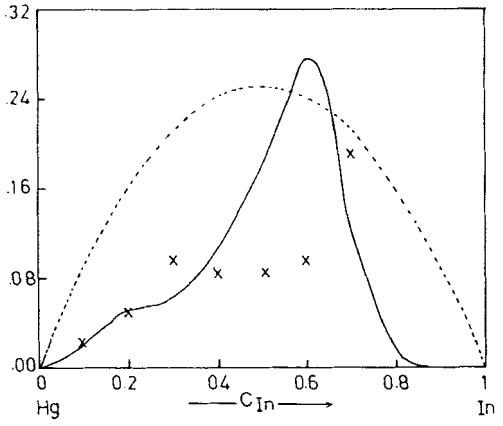

Figure 10 Concentration fluctuation ($S_{cc}(0)$) of $HgIn_6$ (258 K) liquid alloy. Curve points and dotted line have the same meaning as in Figure 4.

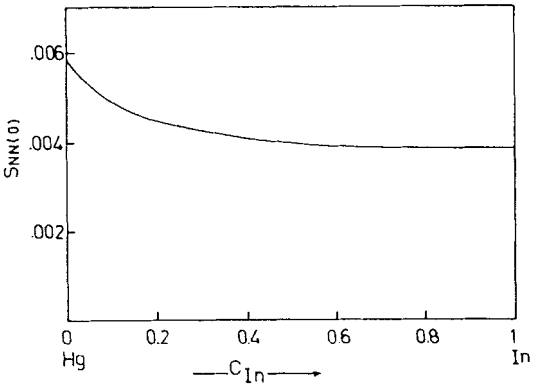

Figure 11 Number-number correlation function of $HgIn_6$ liquid alloy.

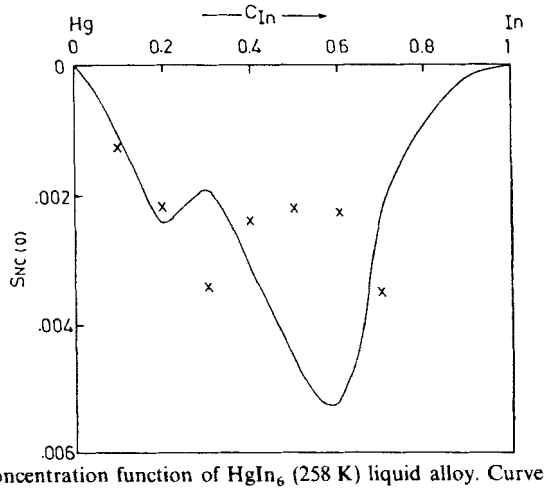

Figure 12 Number concentration function of $HgIn_6$ (258 K) liquid alloy. Curve and points have same meaning as in Figure 4.

5 CONCLUSIONS

In this paper we have studied the thermodynamic properties and the long wavelength correlation functions of HgIn molten alloy and have investigated the formation of HgIn and $HgIn_6$ complexes. The graph of $S_{CC}(0)$ for HgIn and $HgIn_6$ confirms the stability of the HgIn complex and not $HgIn_6$. Furthermore $S_{NN}(0)$, $S_{NC}(0)$ also support the formation of an HgIn complex. It is interesting to note that dependence of w_{ij} on c has been ignored which can affect the value of w_{ij}. Since w_{ij} can substantially change the formation of a complex, possible concentration dependence of w_{ij} is being studied further. The possibility of only one complex formation at a time is considered: the possibility of both complexes coexisting can not be ruled out.

Acknowledgements

The authors wish to thank Prof. R. N. Singh for very useful discussions in the initial stages of the present work. Financial support from U.G.C. is gratefully acknowledged.

References

1. I. S. Jha, R. N. Singh, P. L. Srivastava and N. R. Mitra, *Phil. Mag. B*, **61**, 15 (1990).
2. R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser and K. K. Kelley, Selected values of the thermodynamic properties of binary alloys, ASM, Metal Park, Ohio (1973).
3. T. E. Faber, Introduction to the theory of liquid metals (Cambridge University Press) (1972).
4. A. B. Bhatia and W. H. Hargrove, *Phys. Rev. B*, **10**, 3186 (1974).
5. A. B. Bhatia and D. E. Thornton, *Phys. Rev. B*, **2**, 3004 (1970).
6. R. N. Singh, *Can. J. Phys.*, **65**, 309 (1987).
7. A. B. Bhatia, *Inst. Phys. Conf. Ser.*, **30**, 21 (1977).
8. Ramachandra Rao, R. N. Singh and S. Lele, *J. Non-Cryst. Sol.*, **64**, 387 (1984).