THERMODYNAMIC PROPERTIES OF InNa LIQUID ALLOY

S. K. Chakrabarti*, **I.S. Jha*** and **B. P. Singh****
*Dept. of Physics, M. M. A. M. Campus, Tribhuvan University, Biratnagar, Nepal.
**Dept. of Physics, T. M. Bhagalpur University, Bhagalpur, Bihar, India.

Abstract: The large asymmetry observed in the properties of mixing of indium-sodium liquid alloy is discussed on the basis of quasi-lattice chemical model. A special attention is given to the concentration dependence of free energy of mixing, entropy of mixing and heat of mixing. The results explain the observed asymmetry in the properties of mixing of InNa liquid alloys around equi-atomic composition.

Key words: Complex forming alloys; Binary liquid alloys; Quasi-lattice model; Thermodynamic properties.

1. INTRODUCTION

There are large number of binary alloys the properties of mixing of which are not symmetrical about the equi-atomic composition and deviate maximally from that of the ideal alloys. Some of these alloys also depict metal non-metal transition across a narrow band of concentration.

The anomalous behaviour of these liquid alloys is least understood and demands extensive theoretical investigations. Since long metal physicists—experimentalists[1–5] as well as theoreticians[6–11]—are trying to interpret the physical properties of liquid alloys so that their alloying behaviour could adequately be comprehended.

On the basis of the variation of properties with concentration theoreticians have grouped the liquid alloys into three different major heads : ideal alloys, regular alloys and complex forming alloys. In the last case the properties of mixing are not found to be symmetrical about equi-atomic composition. From a metallurgical standpoint it is instructive to have a good understanding of the properties of liquid alloys because most of the binary solid alloys are formed by cooling from the liquid state.

In the present work we tend to explain the alloying behaviour of indium-sodium liquid alloy on the basis of quasi-lattice chemical model. The concentration dependent properties of InNa liquid alloys are interesting in many ways. The free energy of mixing (G_M), heat of mixing (H_M) and entropy of mixing (S_M) are quite asymmetrical around equi-atomic composition. The phase diagram of InNa alloy suggests that the complexes In_2Na are formed[2].

In Section 2 the general theory of quasi-lattice model is briefly narrated and working expressions are furnished. Section 3 deals with the results and discussion for free energy of mixing, entropy of mixing and heat of mixing of InNa alloy at 713 K. A brief conclusion is provided in Section 4.

2. FORMULATION

The quasi-lattice model as developed by Bhatia and Singh for the binary liquid alloys is a statistical model in which grand partition function is used. The model, in essence, assumes the existence of chemical complexes $A_\mu B_\nu$, where μ & ν are small integers and A & B the constituent species of the alloy :

$$\mu A + \nu B \rightleftharpoons A_\mu B_\nu$$

The grand partition function is solved by assuming that the energy of a given nearest neighbour bond is different if it belongs to the complex than if it does not. With this consideration the expression for excess free energy of mixing comes to be[12]

$$G_M^{xs} = N[c(1-c)\omega + \Phi_{AB}\Delta\omega_{AB} + \Phi_{AA}\Delta\omega_{AA} + \Phi_{BB}\Delta\omega_{BB}], \quad \text{..... (i)}$$

where N is the total number of atoms of A and B in the alloy, 'c' the concentration of A-atoms, ω's the ordering energies and Φ's some constants given by

$$K_B T\Phi_{\mu,\nu} = \Delta\omega_{AB}[2\beta(\mu+1,\nu) - 2\beta(\mu,\nu+1) + \beta(2\mu-1,2\nu) - \beta(2\mu, 2\nu-1)] + \Delta\omega_{AA}[\beta(2\mu-2,2\nu+1) - 2\beta(\mu,\nu+1)] + \Delta\omega_{BB}[2\beta(\mu+1,\nu) - \beta(2\mu+1,2\nu-2)], \quad \text{..... (ii)}$$

K_B being the Boltzmann constant and T the absolute temperature. For the indium-sodium liquid alloy

$A \equiv In, \quad B \equiv Na, \quad \mu = 2, \quad \nu = 1.$

Finding the values of the β-functions in equation (ii), equa-

Author for Correspondence: S. K. Chakrabarti, Dept. of Physics, M. M. A. M. Campus, Tribhuvan University, Biratnagar, Nepal. E-mail: skc_2007@yahoo.com

tion (i) reduces to

$$G_M^{xs} = N\left[\omega c(1-c) + \Delta\omega_{AB}\left(\frac{1}{6}c + c^2 - \frac{5}{3}c^3 + \frac{1}{2}c^4\right) + \Delta\omega_{AA}\left(-\frac{1}{4}c + \frac{1}{2}c^2 - \frac{1}{4}c^4\right)\right] \quad \text{.... (iii)}$$

Hence, the free energy of mixing of a complex forming binary liquid alloy,

$$G_M = G_M^{xs} + RT[c\ln c + (1-c)\ln(1-c)], \quad \text{..... (iv)}$$

where R is the universal gas constant.

The excess entropy of mixing is given by

$$S_M^{xs} = -\left(\frac{dG_M^{xs}}{dT}\right)_P$$

$$= -N\left[\frac{d\omega}{dt}\Phi(c) + \frac{d}{dt}(\Delta\omega_{AB})\Phi_{AB}(c) + \frac{d}{dt}(\Delta\omega_{AA})\Phi_{AA}(c) + \frac{d}{dt}(\Delta\omega_{BB})\Phi_{BB}(c)\right] \quad \text{... (v)}$$

So, the entropy of mixing of such a binary liquid alloy,

$$S_M = S_M^{xs} - R[c\ln c + (1-c)\ln(1-c)]. \quad \text{..... (vi)}$$

Now, the heat of mixing can be found out by using equations (iii) and (v) :

$$H_M = G_M^{xs} + T S_M^{xs} \quad \text{..... (vii)}$$

3. RESULTS AND DISCUSSION

3.1 Free energy of mixing

The values of interaction parameters are determined from the experimental values[3] of G_M in the concentration range from 0.1 to 0.9. In this course we find that $\Delta\omega_{AA}$ has relatively minor influence. So, we set $\Delta\omega_{AA}$=0. The remaining two parameters are found out to be

$$\frac{\omega}{K_B T} = 0.7 \quad \text{and} \quad \frac{\Delta\omega_{AB}}{K_B T} = -2.2$$

at T=713 K. The theoretical and experimental values of the free energy of mixing are in well agreement vide G_M/RT–c_{In} curve in Fig–1. Both the experimental and theoretical values of G_M show minimum at c_{In}=0.57.

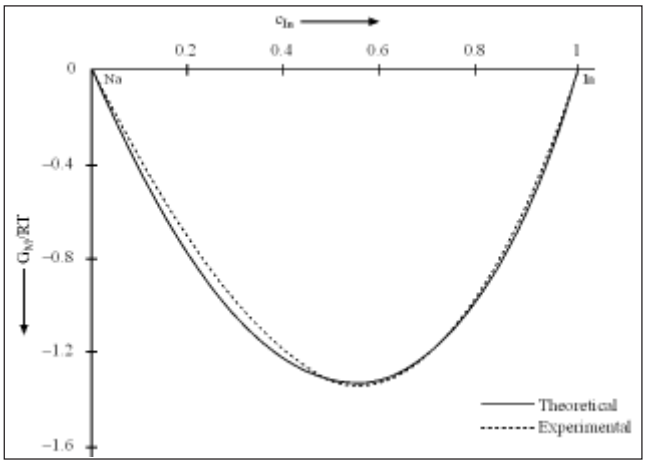

Fig 1: G_M/RT–c_{In} curve for InNa liquid alloy at 713 K

3.2 Entropy of mixing

The observed values[3] of S_M are used to obtain the temperature derivative of interaction parameters. We have found out:

$$\frac{1}{K_B}\frac{d\omega}{dT} = 6.3, \quad \frac{1}{K_B}\frac{d}{dT}(\Delta\omega_{AB}) = -3.6 \quad \text{and} \quad \frac{d}{dT}(\Delta\omega_{BB}) \approx 0$$

The concentration dependence of S_M/R at 713 K. is plotted in Fig–2. Both the theoretical and experimental values of S_M are positive in the sodium-rich region i.e. $0 < c_{In} \leq 0.32$. Also S_M is positive in the indium-rich region i.e. $0.73 \leq c_{In} < 1$. But our theoretical values are negative in the region $0.39 < c_{In} < 1$.

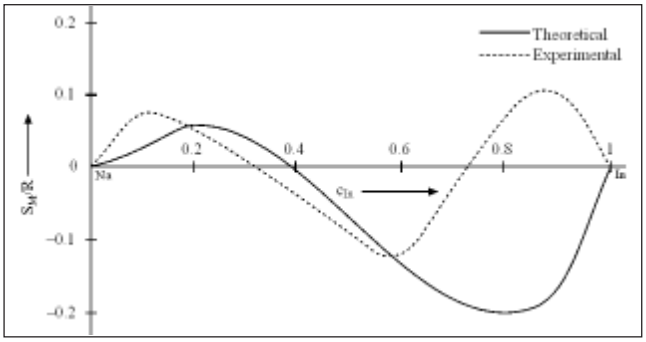

Fig 2: S_M/R–c_{In} curve for InNa liquid alloy at 713 K

3.3 Heat of mixing

The heat of mixing of the indium-sodium alloy has been computed as a function of concentration from equation (vii). The plot of H_M/RT versus c_{In} at 713 K. is depicted in Fig–3 for both the theoretical and experimental values[3], which show good agreement. The theoretical value of H_M is minimum at c_{In}=0.62 while experimentally it is found to be minimum at c_{In}=0.59.

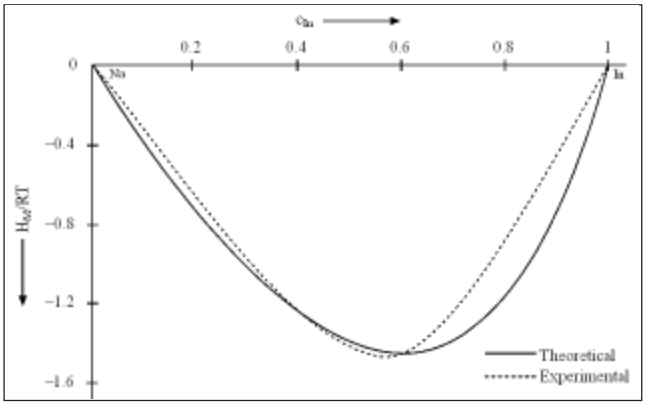

Fig 3: H_M/RT–c_{In} curve for InNa liquid alloy at 713 K

4. CONCLUSION

The alloying behaviour of InNa liquid alloy is well explained by the above theoretical model. Only in the indium-rich region some marked deviations are seen between the theoretical and experimental values of entropy of mixing.

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