Journal of Molecular Liquids 167 (2012) 52–56

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Structural and energetic anomaly in liquid Na–Sn alloys

D. Adhikari [a,b,*], B.P. Singh [a], I.S. Jha [b]

[a] Univ. Dept. of Physics, T. M. Bhag. University, Bhagalpur, Bihar, India
[b] Dept. of Physics, M.M.A.M. Campus (Tribhuvan University), Biratnagar, Nepal

ARTICLE INFO

Article history:
Received 28 September 2011
Received in revised form 14 November 2011
Accepted 23 December 2011
Available online 9 January 2012

Keywords:
Binary alloy
Na–Sn alloy
Complexes
Interaction energies

ABSTRACT

The alloying behaviour of Na–Sn liquid alloys at 773K has been studied by using regular associated solution model. This model has been utilized to determine the complex concentration in a regular associated solution of Na and Sn. We have then used the complex concentration to calculate the free energy of mixing (G_M), enthalpy of mixing (H_M), entropy of mixing (S_M), concentration fluctuations in long wavelength limit ($S_{CC}(0)$), the Warren Crowley short-range parameter (α_1) and ratio of mutual and intrinsic diffusion coefficients (D_M/D_{id}). The analysis suggests that heterocoordination leading to the formation of complex Na_3Sn is likely to exist in the liquid and is of a strongly interacting nature. The theoretical analysis reveals that the pairwise interaction energies between the species depend considerably on temperature and the alloys are more ordered towards intermediate region.

1. Introduction

The study of the mixing behaviour of liquid alloys is of immense importance for physicists, chemists and engineers for designing and exploring new materials. Thus determination of different properties of liquid alloys, such as thermodynamic, surface, structural, electrical, magnetic properties has been the subjects of active research in metallurgical science for many years. But understanding the properties of liquid alloys is much more difficult than that of crystals due to the presence of strong interactions among the particles and their state of disorder in liquid state. Several theoretical models [1–12] have long been employed to solve the complexities of obtaining different properties of binary liquid alloys. In this work we have studied the thermodynamic and structural properties of Na–Sn liquid alloy at 773K on the basis of regular associated solution model.

In regular associated solution model, strong associations among the constituent species are assumed to exist in the liquid phase of binary alloys close to the melting temperature. Due to the strong associations present in the solution, complexes are formed. Thus the binary alloys in a liquid phase can be considered as a ternary mixture of unassociated atoms of components and complexes, all in chemical equilibrium. But the interactions between both the unassociated atoms and the complex are considered no longer equal and hence unassociated atoms do not interact equally with the complex.

Several workers [13–21] have theoretically and experimentally tried to understand different properties of Na–Sn system in liquid state. Asymmetry in various properties of mixing of molten Na–Sn alloys is noticed around equiatomic composition. The size factor ($\Omega_{Na}/\Omega_{Sn} = 1.45$; Ω being the atomic volume) and electronegativity difference ($E_{Sn} - E_{Na} = 1.03$) are not large enough to account for the anomalous behaviour of mixing properties. The phase diagram shows the existence of several intermediate phases in the liquid state of Na–Sn alloys which has been confirmed by several workers [19,22,23]. Several pieces of experimental evidence clearly demonstrate that the asymmetric behaviour for a large number of liquid alloys occur at or near the stoichiometric composition where stable intermetallic compound exist in the solid phase. It is, therefore, natural to propose that the 'chemical complexes' or psedomolecules' exist in the liquid phase near the melting temperature. From the Na–Sn phase diagram (see refs. suggested above), the Na_9Sn_4 intermetallic compound exists up to 478 °C, and it melts congruently at that temperature. The curve of the enthalpy of mixing of Na–Sn solutions at 500 °C exhibits the minimum value at 43 at.% Sn [22,23]. These findings are corroborated by neutron diffraction measurements [18].Taking into account that in the liquid phase the irregularities (due to strong interactions in the system in questions) on the property-curves sometimes are often shifted with respect to the exact composition of an energetically favoured intermetallic compound, the Na_9Sn_4 (31 at.%Sn) can be approximated by A_3B stoichiometry (Na_3Sn, with 25 at.%Sn), because none of the models used takes into account the stoichiometry A_9B_4 (always the stoichiometric coefficients are small integers). Thus we consider Na_3Sn phase to describe the thermodynamic and structural properties of Na–Sn liquid alloy at 773K.

The layout of the paper is as follows. In Section 2, the theoretical basis of our work is presented. Section 3 gives the results and discussion of this work. Finally, the conclusions are outlined in Section 4.

* Corresponding author at: Univ. Dept. of Physics, T. M. Bhag. University, Bhagalpur, Bihar, India.
E-mail address: adksbdev@yahoo.com (D. Adhikari).

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doi:10.1016/j.molliq.2011.12.010

2. Theory

Let the solution of the binary alloy A–B (=Na–Sn) consists of n_1 atoms of species A and n_2 atoms of species B. Following Lele and Ramchandrarao [24], it is assumed that chemical complexes ApB ($A_pB \Leftrightarrow pA+B$) exist in the melt, where p is a small integer which is usually determined from the compound –forming concentration (= p/(p+1)) in the solid state. Because of the existence of the compound, liquid alloys are supposed to be composed of three species, namely, monomers A (=Na), B (=Sn) and complex ApB (=Na_3Sn) in equilibrium, where p=3. Let the concentration of A, B and ApB species be n_A, n_B, and n_{ApB} moles respectively. In the partially associated solution the formation of n_{ApB} complex requires $n_1 = n_A + pn_{ApB}$ and $n_2 = n_B + n_{ApB}$ for conservation of mass. When there is association, the thermodynamic behaviour of complexes A and B components is governed by their true mole fractions x_A, x_B and x_{ApB} (where $x_A = \frac{n_A}{n_A+n_B+n_{ApB}}$ etc.) rather than their gross mole fraction x_1 and x_2, (where $x_1 = \frac{n_1}{n_1+n_2}$ etc.).

Using above relations the two sets of mole fractions are related to each other by the relations

$$x_A = x_1 - px_2x_{ApB},\ x_B = x_2 - (1-px_2)x_{ApB} \tag{1}$$

Progonine and Defay [25] have shown that in associated solutions, the gross chemical potentials of components 1 and 2 are equal to the chemical potentials of the monomeric species A and B. Following Jordan [26] the activity coefficients γ_A, γ_B and γ_{ApB} of monomers and complex can be expressed in terms of pairwise interaction energies through

$$RT\ln\gamma_A = x_B^2\omega_{12} + x_{ApB}^2\omega_{13} + x_Bx_{ApB}(\omega_{12} - \omega_{23} + \omega_{13}) \tag{2a}$$

$$RT\ln\gamma_B = x_{ApB}^2\omega_{23} + x_A^2\omega_{12} + x_Ax_{ApB}(\omega_{23} - \omega_{13} + \omega_{12}) \tag{2b}$$

$$RT\ln\gamma_{ApB} = x_A^2\omega_{13} + x_B^2\omega_{23} + x_Bx_A(\omega_{13} - \omega_{12} + \omega_{23}) \tag{2c}$$

where ω_{12}, ω_{13} and ω_{23} are interaction energies for the species A, B ; A, A_pB and B, A_pB respectively, T the temperature and R stands for the universal gas constant.

The equilibrium constant for the reaction $ApB \Leftrightarrow pA + B$ is given

$$k = \frac{x_A^p x_B \gamma_A^p \gamma_B}{x_{ApB}\gamma_{ApB}}. \tag{3}$$

Thus, using Eqs. (1)–(3), one gets

$$\ln k = \ln\left(\frac{x_A^p x_B}{x_{ApB}}\right) + \frac{\omega_{12}}{RT}[px_B(1-x_A) + x_A] + \frac{\omega_{13}}{RT}\left[px_{ApB}(1-x_A) - x_A\right] + \frac{\omega_{23}}{RT}\left[x_{ApB}(1-px_B) - x_B\right]. \tag{4}$$

Now using the equations listed above the free energy G_M is given by

$$G_M = \frac{1}{\left(1+px_{ApB}\right)}\left(x_Ax_B\omega_{12} + x_Ax_{ApB}\omega_{13} + x_Bx_{ApB}\omega_{23}\right) + \frac{RT}{\left(1+px_{ApB}\right)} \times \left(x_A\ln x_A + x_B\ln x_B + x_{ApB}\ln x_{ApB}\right) + \frac{x_{ApB}}{\left(1+px_{ApB}\right)}RT\ln k. \tag{5}$$

Once the expressions for G_M is obtained, other thermodynamic and microscopic functions follow readily. Heat of mixing (H_M), entropy of mixing(S_M) and concentration fluctuations in the long-wavelength limit ($S_{CC}(0)$) are related to G_M through standard thermodynamic relations

$$H_M = G_M - T\left(\frac{\partial G_M}{\partial T}\right)_P \tag{6}$$

$$S_M = \frac{H_M - G_M}{T} \tag{7}$$

$$S_{CC}(0) = RT\left(\partial^2 G_M/\partial C^2\right)_{T,P}^{-1} \tag{8a}$$

$$S_{CC}(0) = (1-C)a_1(\partial a_1/\partial C)_{T,P}^{-1} = Ca_2(\partial a_2/\partial(1-C))_{T,P}^{-1} \tag{8b}$$

where C (= x_{Na}) is concentration of A component in the alloy. Eq. (5) is used in Eqs. (6) and (8a), we obtained expressions for $H_M$and $S_{CC}(0)$ as

$$H_M = \frac{1}{\left(1+px_{ApB}\right)}\left(x_Ax_B\omega_{12} + x_Ax_{ApB}\omega_{13} + x_Bx_{ApB}\omega_{23}\right) - \frac{T}{\left(1+px_{ApB}\right)} \times \left(x_Ax_B\frac{\partial\omega_{12}}{\partial T} + x_Ax_{ApB}\frac{\partial\omega_{13}}{\partial T} + x_Bx_{ApB}\frac{\partial\omega_{23}}{\partial T}\right) - \frac{x_{ApB}}{\left(1+px_{ApB}\right)}RT^2\frac{d\ln k}{dT} \tag{9}$$

$$S_{CC}(0) = \left\{\frac{1}{\left(1+px_{ApB}\right)}\left[\frac{2}{RT}\left(x_A'x_B'\omega_{12} + x_A'x_{ApB}'\omega_{13} + x_B'x_{ApB}'\omega_{23}\right) + \left(\frac{x_A'^2}{x_A} + \frac{x_B'^2}{x_B} + \frac{x_{ApB}'^2}{x_{ApB}}\right)\right]\right\}^{-1}. \tag{10}$$

Here, $\frac{\partial^2 G_M}{\partial C^2} > 0$ for $\frac{\partial G_M}{\partial C} = 0$where prime denotes the differentiations with respect to concentration and x_A' and x_B' are determined by using Eq. (1). x_{ApB}' is determined using the Eq. (4) and the condition $\frac{d\ln k}{dC} = 0$ [27,28]. It may be noted that the factor $(1+px_{ApB})^{-1}$ which appears as a coefficient of all terms containing $x_A, x_B$and x_{ApB} in the Eqs. (5), (9) and (10), is a result of the change in the basis for expressing mole fractions of species A, B and ApB from that used for x_1 and x_2.

The $S_{CC}(0)$ can be directly determined using Eq. (8b) [29]. This is usually considered as the experimental value.

In order to quantify the degree of local order in the liquid alloy, Warren-Cowley short-range parameter α_1 [30,31] can be estimated from the knowledge of concentration–concentration structure factor $S_{CC}(q)$ and the number-number structure factor $S_{NN}(q)$. However, in most diffraction experiments these quantities are not easily measurable for all kinds of binary liquid alloy. On the other hand α_1 can be estimated from the knowledge of $S_{CC}(0)$ [32,33]

$$\alpha_1 = \frac{S-1}{S(Z-1)+1}, \qquad S = \frac{S_{CC}(0)}{S_{CC}^{id}(0)};\ S_{CC}^{id} = x_1x_2 \tag{11}$$

where Z is coordination number and Z=10 is taken for our calculation. We note that varying the value of Z does not have any effect on the position of the minima of α_1; the effect is to vary the depth while the overall feature remains unchanged.

The mixing behaviour of the alloys forming molten metals can also be studied at the microscopic level in terms of the coefficient of diffusion. The $S_{CC}(0)$ and diffusion coefficients can be related using Darken thermodynamic equation for diffusion [34,35] as follows,

$$\frac{D_M}{D_{id}} = \frac{x_1x_2}{S_{CC}(0)} \tag{12}$$