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Size Sensitive Transport Behavior of Liquid Metallic Mixtures

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ABSTRACT

We have used a formalism that connects thermodynamic and transport properties. The formalism has been used to calculate the Gibb's free energy of mixing, concentration fluctuations in the long wavelength limit, diffusion coefficients and viscosity in Cu-Tl, Cu-Pb and Sn-Tl binary liquid alloys at 1573K, 1473K and 723K respectively with aid of size effect and no size effect. Our calculations show that appreciable size ratio has more effects on the transport properties as compared to thermodynamic properties of homo-coordinated liquid alloys Cu-Tl, Cu-Pb and Sn-Tl.

Keyword: Homo-coordinated alloys, size sensitive, diffusivity, viscosity

INTRODUCTION

There are various empirical models which have been used to study the structure and thermodynamics of the liquid binary alloys since midway of last century. However, the difficult task for establishing an empirical model that will connect thermodynamic and transport properties of binary liquid alloys was accepted by Singh and Sommer (1998). They gave essential connection between thermodynamics and transport properties through an empirical formula, which was about the first innovator work in providing the aforesaid. In this model, they were able to connect two transport quantities as like viscosity (η) and diffusivity (D) for binary liquid alloys with thermodynamic quantities like as Gibb's free energy of mixing (G_M) and the concentration fluctuation in the long wavelength limit ($S_{cc}(0)$). In essence, they related these quantities by using enthalpic and entropic (size) contributions to G_M. This model has been applied at first by Akinlade *et al.* (1998) to two homo-coordinating alloys, Bi-Zn and Cu-Bi and later Awe (2010) applied it for four liquid alloys. This paper used the same empirical model of thermodynamic equation of diffusion to explore the effect of size on the transport properties of the alloys Cu-Tl, Cu-Pb ans Sn-Tl (Singh & Sommer 1998, Darken 1953). Our choice of first two alloys was based on the fact that they are examples of alloys where size mismatch between atom A and B in each of the alloys is considered to be significant (Singh 1987). That is the size difference between atom A and B does not lies within 50 percent and, hence, the difference is not negligible, i.e. at the melting points, in Cu-Tl, Tl atom is 2.42 times bigger than the Cu-atom and in Cu-Pb, Pb atom is 2.57 times bigger than Cu-atom (Iida *et al.* 1988). But third alloys Sn-Tl have negligible size difference between constituent atoms. In addition we are also aware that the three alloys represent the distinct classes of binary liquid alloys, namely, class of alloys that exhibit positive deviation from raoult's law of linearity, known as homo-coordinated or segregating alloys. Another reason for selecting to work on these alloys is that each of the alloys has either an interesting features or is industrially relevant. This paper also focuses on formalism for each of thermodynamic, microscopic and transport properties of interest.

FORMALISM

Thermodynamic and microscopic properties: Gibb's free energy of mixing and concentration fluctuation in long wavelength limit

Thermodynamic properties provide information on the interaction, stability and bonding strength among the constituent atoms in the alloys. The microscopic properties are useful in obtaining the microscopic information on structure of molten alloys. We shall employ the expressions for free energy of mixing (G_M) and concentration fluctuation in long wavelength limit ($S_{cc}(0)$) which incorporate the two fitting parameters (W and γ), are needed to calculate the transport properties. These expressions are based on Guggenheim's theory of mixture and Flory's model (Guggenheim 1952, Flory 1942). The equations which are used to compute G_M and $S_{cc}(0)$ for each of three alloys when size mismatch is taken into consideration (WSE) are followed by Flory's model (Flory 1942) as

$$\frac{G_M}{RT}^{WSE} = c_A \ln(1-\beta) + c_B \ln\beta + c_A W\beta \quad (1)$$

where, $\beta = \frac{\gamma c_B}{c_A + \gamma c_B}$, $W = \Omega_A \left(\frac{\omega}{k_B T}\right)$

$$S_{cc}(0)^{WSE} = \frac{c_A c_B}{1 - c_A c_B f(\gamma, W)} \quad (2)$$

Where $\gamma = \Omega_B / \Omega_A$, size ratio of the constituent atoms. However, for the purpose of completeness we have as well computed the G_M and $S_{cc}(0)$ for each of the three alloys where size mismatch are immaterial (NSE) using the following equations in simple statistical model (Singh *et al.* 2015, Koirala *et al.* 2014)

$$\frac{G_M}{RT}^{NSE} = c_A \ln c_A + c_B \ln c_B + c_A c_B \frac{\omega}{k_B T} \quad (3)$$

$$S_{cc}(0)^{NSE} = \frac{c_A c_B}{1 - c_A c_B \left(\frac{2\omega}{k_B T}\right)} \quad (4)$$

Transport properties: diffusion and viscosity

Essentially, viscosity and diffusion measurements are employed by theoreticians as well as experimentalists to extract information about alloying or atomic association in liquids as they shed light on the understanding of the mixing behavior and can be used to ascertain the stoichiometric composition of associates that are formed (Singh & March 1995, Anusionwu *et al.* 1998, Novakovic *et al*. 2004). With a view to investigate the effect of size on the transport properties of the alloys of present interest we have attempted to calculate their ratio of the mutual and self diffusion coefficients, D_M/D_S (or D_M/D_{id}) as well as their viscosities using Darken's thermodynamic equation of diffusion as given by Novakovic *et al.* (2004) and the model of Singh and Sommer (1998) respectively. The relationship between Darken's thermodynamic equation of diffusion and concentration-concentration fluctuation in long wavelength limits (Darken & Gurry 1953) is given as

$$\frac{D_M}{D_{id}} = \frac{S_{cc}^{id}(0)}{S_{cc}(0)} \quad (5)$$

where D_M is the mutual or chemical diffusion coefficient and D_{id} is the self or intrinsic coefficient for ideal mixture while $S_{cc}^{id}(0)$ is the ideal concentration-concentration fluctuation. The ratio D_M/D_{id} indicates the mixing nature of molten alloys; $D_M / D_{id} < 1$ indicates the tendency of homo-coordination while $D_M/D_{id} > 1$ indicates the tendency of hetero-coordination and D_M/D_{id} approaches 1 for ideal mixing. Consequently, the highest peak on the diffusivity curve (i.e. plot of D_M/D_{id} against concentration of the species) suggest the presence of maximum chemical order in the liquid alloy system and the composition of the most probable associates to be formed in the liquid phase (Novakovic *et al*. 2004).

In order to investigate the effect of size mismatch on the diffusivity of each of the two alloys we put Eqs. (2) and (4) in turns in Eq. (5) so as to obtain the following two equations which respectively represent the diffusivity when the size mismatch is taken into consideration (WSE) and the diffusivity when size mismatch is immaterial (NSE):

$$\frac{D_M}{D_{id}}^{WSE} = 1 - c_A c_B f(\gamma, W) \quad (6)$$

$$\frac{D_M}{D_{id}}^{NSE} = 1 - c_A c_B \left(\frac{2\omega}{k_B T}\right) \quad (7)$$

The relationship between the viscosity (η) and chemical diffusion coefficient (D_M) is provided by several researchers (Singh & Sommer 1998, Novakovic *et al*. 2004, Anusionwu *et al.* 1998) as:

$$\eta = \frac{k_B T}{D_M}\left(\frac{c_A}{m_B} + \frac{c_B}{m_A}\right)\psi \quad (8)$$

where m_i (i= A or B) is a parameter that depends on the size and shape of the particle; k_B and T are the respectively Boltzmann's constant and absolute temperature; c_A and c_B are the concentrations for A and B atom respectively. Eq. (8) can be re-written as

$$\eta = \eta^0 \psi \quad (9)$$

$$\text{where } \eta^0 = \frac{k_B T}{D_M}\left(\frac{c_A}{m_B} + \frac{c_B}{m_A}\right) \quad (10)$$

The expression of ψ that incorporates both enthalpic and entropic effect is given by Singh and Sommer (1998) as:

$$\psi = 1 - c_A c_B f(\gamma, W) \quad (11)$$

$$\text{with } f(\gamma, W) = \frac{2\gamma^2 W - (\gamma-1)^2 (c_A + \gamma c_B)}{(c_A + \gamma c_B)^3} \quad (12)$$

From Eqs. (8) and (11),one obtains the expression for viscosity

$$\frac{\Delta\eta}{\eta}^{WSE} = -c_A c_B f(\gamma, W) \quad (13)$$

where $\Delta\eta = \eta - \eta^o$, deviation in η.

According to Singh and Sommer (1998) when only enthalpic effect is considered, the expression for ψ is given as

$$\Psi = 1 - c_A c_B \left(\frac{2\omega}{k_B T} \right) \quad (14)$$

where ω is the ordering energy.

When Eqs.(8) and (14) are combined, we obtain an expression as

$$\frac{\Delta\eta}{\eta}^{NSE} = - c_A c_B \left(\frac{2\omega}{k_B T} \right) \quad (15)$$

RESULTS AND DISCUSSION

For the theoretical calculation the necessary input parameters are W and γ. Although, the emphasis in this paper is on transport properties, we nevertheless need to calculate two of the bulk properties (G_M and $S_{cc}(0)$) so that we can obtain the two fitting parameters(i.e.W, γ). We have no information on the experimental values of the transport properties while we have experimental data on G_M and $S_{cc}(0)$. In this light we shall employ the expressions for G_M and $S_{cc}(0)$ which incorporate the two fitting parameters. Eqs. (1) and (2) have been used simultaneously to obtain the fitting parameters that give a good overall fit for G_M and $S_{cc}(0)$. The values obtained are shown in table 1.Experimental values of G_M for the alloys obtained directly from Hultgren *et al.* (1973). The values of $S_{cc}(0)$ are obtained via the values of experimental activity (Hultgren *et al.* 1973) as given by

$$S_{cc}(0) = c_B a_A \left(\frac{\partial a_A}{\partial c_A} \right)^{-1} = c_A a_B \left(\frac{\partial a_B}{\partial c_B} \right)^{-1} \quad (16)$$

where a_A and a_B are the observed chemical activities of atom A and B respectively. The values of fitting parameters obtained as shown in Table 1 are quite reliable since Figs. 1 and 2 indicate that we have a good fits for G_M and $S_{cc}(0)$ for two alloys Cu-Tl and Cu-Pb with aid of WSE but for Sn-Tl good fit is obtained with aid of NSE. A comparison of the plots of WSE and NSE in each of the figures show that the degree of asymmetry in Cu-Tl (γ=2.42) is more than that of Cu-Sn (γ=2.57). This implies that the effect of size mismatch on homo-coordinated alloys is inversely proportional to the size ratio. In addition, we observe that in these figures the plot of WSE shows that in the homo-coordinated alloys there is crossover from a decrease in the degree of homo-coordination to an increase in the degree of homo-coordination. But the asymmetry is negligible in case of alloy Sn-Tl whose size ratio is small (γ=1.06). In that case, both curves with aid of WSE and NSE are very close to each other and the experimental and theoretical values are in good agreement throughout whole concentration (Figs.1 and 2(c)). This result implies that the mixing behavior of liquid alloys in the framework of simple statistical model (NSE) is not sensitive to size mismatch. It concluded that NSE formulation is superior to WSE formulation or Flory's model if size ratio of the constituents is very small.

Table 1. Essential fitting parameters for the calculation of transport properties for Cu-Tl, Cu-Pb and Sn-Tl

Alloys	Temperature	$(\omega / k_B T)^*$	γ^{**}
Cu-Sb	1573K	1.47	1.89
Cu-Sn	1473K	1.35	1.60
Sn-Tl	723K	0.76	1.06

* for both WSE and NSE & ** fitting values

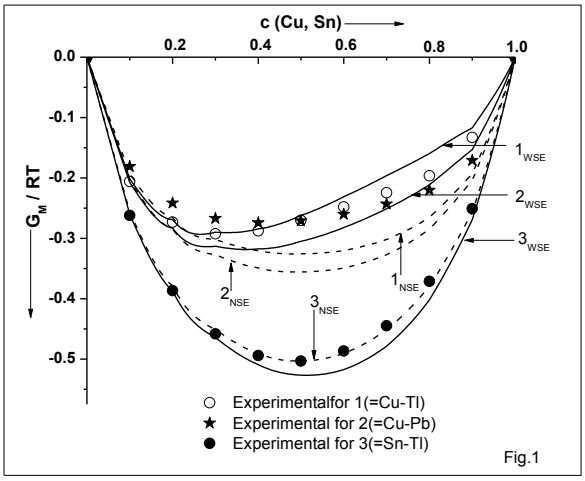
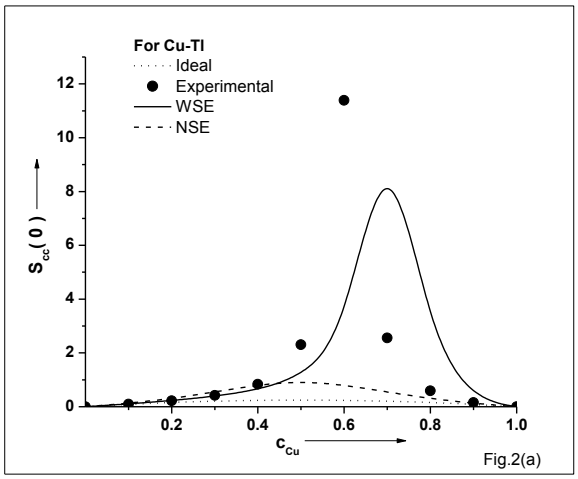
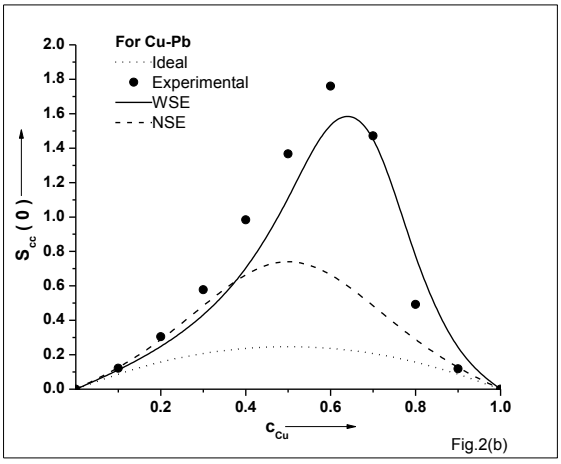


Fig.1. Free energy of mixing (G_M/RT) Vs concentration (c) for Cu-Tl, Cu-Pb and Sn-Tl liquid alloys at 1573K, 1473K and 723K respectively. Circles, Stars and Dark circles represent experimental values (Hultgren et al)] for Cu-Tl, Cu-Pb and Sn-Tl respectively; WSE means with size effect and NSE means no size effect.

The plots of graph of ratio of diffusion coefficients against concentration for each of the three alloys are shown in Fig. 3. In all alloys, D_M/D_{id} is less than one, indicates that alloys are homo-coordinated, as earlier confirmed in the bulk properties calculations. A comparison of the plots WSE and NSE reveals that the effect of size mismatch on Cu-Tl and Cu-Pb is to reduce the degree of homo-coordination in the range of composition $0 \leq x_{Cu} < 0.44$ and increase the degree of homo-coordination in the rest of the composition. We also observe that the effect of size mismatch on the diffusivity of Cu-Tl is more than that on Cu-Pb, since the asymmetry caused by size mismatch is more

pronounced in Cu-Tl than in Cu-Pb. Also, in view of fact that size ratio of Cu-Tl is greater than Cu-Pb, we infer that there is direct relationship between size mismatch and diffusivity of homo-coordinated alloys. But asymmetric result is not found in the case of alloy Sn-Tl, which causes of small size ratio of the components. From the plot in Fig. 4, same type of result is obtained. A perusal of the plots in Figs. 3 and 4 for the alloys shows that the plots NSE are symmetrical about equi-atomic composition while there is significant asymmetry in WSE plots due to size mismatch. In addition, we observe that asymmetry in Cu-Tl is more than in Cu-Pb and Sn-Tl. This is in agreement with the statement that asymmetry in $\Delta\eta$ about equi-atomic composition is induced by size factors (Singh & Sommer 1998).





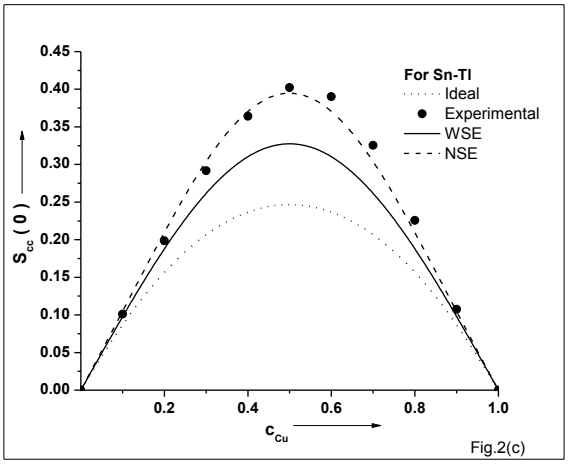
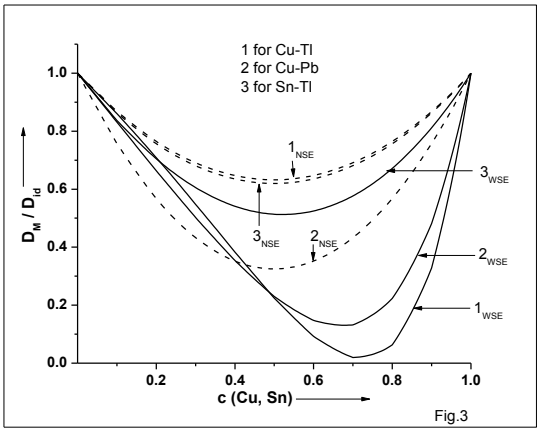


Fig. 2. Concentration fluctuation in long wavelength limits ($S_{cc}(0)$) Vs concentration (c). (a) For Cu-Tl at 1573K. (b) For Cu-Pb at 1473K. and (c) For Sn-Tl at 723K



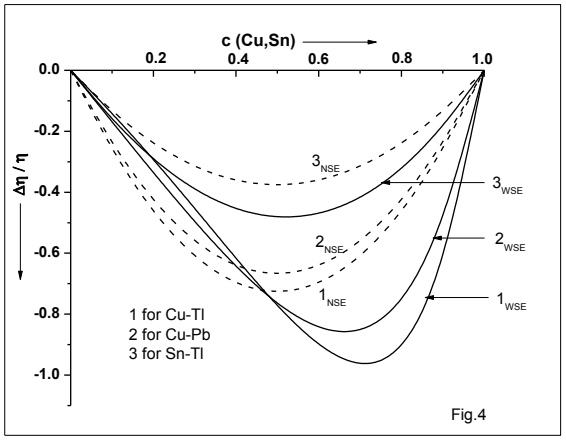


Fig. 3. Diffusion coefficient ratio (D_M/D_{id}) Vs concentration (c) for Cu-Tl, Cu-Pb and Sn-Tl liquid alloys at 1573K, 1473K and 723K respectively. WSE means with size effect and NSE means no size effect.

Fig. 4. Deviation of viscosity from ideal values ($\Delta\eta/\eta^0$) Vs concentration (c) for Cu-Tl, Cu-Pb and Sn-Tl liquid alloys at 1573K, 1473K and 723K respectively. WSE means with size effect and NSE means no size effect.

CONCLUSIONS

Our studies of size mismatch effects on the thermodynamic, structural and transport properties of Cu-Tl at 1190K, Cu-Pb at 1400K and Sn-Tl at 723K have led to the following submissions:

- The size mismatch is either solely or at least majorly responsible for the asymmetry and shaping of the asymmetry in each of the alloys.
- The degree of asymmetry of transport properties caused by size mismatch is inversely proportional to the magnitude of size mismatch in the homo-coordinated alloys.
- Size mismatch has a crossover effect on the transport properties of the alloys studied: it reduces the degree of homo-coordination in Cu-Tl and Cu-Pb in the range of composition $0 \leq x_{Cu} < 0.44$ and the increases the degree of homo-coordination in the rest of composition.
- The mixing behavior of liquid alloys in the framework of simple statistical model (NSE) is not sensitive to size mismatch if size ratio of the constituents is very small.
- This work suggests that the presented model and formulation can be used to study the size mismatch effects on the transport properties of binary liquid alloys on the basis thermodynamic data.

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