Application of the molecular interaction volume model to the assessment of thermodynamic properties of liquid Zn-Bi alloys

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Abstract

This paper is an attempt to extract useful thermodynamic information from the experimental activity of zinc in Zn-Bi binary liquid alloy at different temperatures. The molecular interaction volume model (MIVM) was adopted to calculate a number of temperature dependent thermodynamic functions, including activity, free energy of mixing, concentration fluctuations in the long-wavelength limits, and diffusion. The reasonable agreement of the modeled thermodynamic parameters with the existing experimental data verified that the MIVM is quite convenient and reliable in the assessment of the thermodynamic properties of binary liquid alloys.

K e y   w o r d s: Zn-Bi, thermodynamic properties, molecular interaction volume model

1. Introduction

Most of the alloys are usually solidified from their liquid phases. Liquid alloys generate broad interest to researchers in materials, physics, and chemistry, since their atomic arrangements are significantly varied, which are heterocoordinated or homocoordinated. The liquid immiscible alloys had been experimentally investigated for 70 years. However, the complexity in the properties of mixing of binary liquid alloys is still less understood although some empirical and semiempirical models [1–5] have been proposed. Therefore, the study of the properties of binary liquid alloys demands extensive theoretical investigations at the microscopic level.

Elements Bi and Zn are the key compositions of the majority of multicomponent lead-free solders. The liquid binary system Bi-Zn separates forming Bi-rich and Zn-rich phases within a certain range of temperatures and concentrations, which was experimentally evidenced by the temperature variation of physical properties such as viscosity, sound velocity, and thermodynamics [6–8]. The shape of the miscibility gap is remarkably flat and asymmetric, which enhanced difficulties during theoretical analysis [9]. There is some

theoretical evidence from the points of quasi-lattice theory considering the combined effect of size ratio, entropic and enthalpic effect [10], and the perturbation approach that involves both energy of mixing and entropy of mixing [11].

In the study of multicomponent alloys, the MIVM is more popular, known for its reliability, its statistical thermodynamic origin and the fact that its application requires few parameters [12–15]. In this paper we have used the molecular interaction volume model, which is explained in the next sections, to predict the values of the thermodynamic and structural properties of Zn-Bi liquid alloys at different temperatures.

2. Molecular interaction volume model

2.1. Molar excess Gibbs energy of mixing and activity

MIVM is based on the physical perspective of movement of liquid molecules which is known to be unlike that of solid or gas. The molecules of a liquid migrate non-randomly from one molecular cell to another unlike in gases and solids where molecules re-

spectively move continuously in the irregular pattern and constantly vibrate at lattice sites [16, 17]. From the nature of liquid molecular motion which allows each molecule to move into an adjacent hole as a central molecule, it is assumed that liquid molecules can move freely through a cell space, and the molecular interaction separation tending towards the cell diameter at certain temperature [18]. MIVM is built on the assumption that neighboring atoms are relative to each other, exchangeable, mobile and possess similar cells [16, 17].

Based on the non-random migration of liquid atoms, the MIVM is derived from statistical thermodynamics by Tao [12]. This model takes into account physical properties of the pure metals constituting the alloy, namely the molar volume, V_{m}, and the first coordination number, Z, in the liquid state, which are temperature dependent [19, 20]. The molar excess Gibbs energy G^{E} of the liquid mixture i–j is given by

$$
G^{\mathrm{E}} = RT \left(x_i \ln \frac{V_{\mathrm{m}i}}{x_i V_{\mathrm{m}i} + x_j V_{\mathrm{m}j} B_{ji}} + \right.
$$
$$
+ x_j \ln \frac{V_{\mathrm{m}j}}{x_j V_{\mathrm{m}j} + x_i V_{\mathrm{m}i} B_{ij}} -
$$
$$
\left. - \frac{x_i x_j}{2} \left(\frac{Z_i B_{ji} \ln B_{ji}}{x_i + x_j B_{ji}} + \frac{Z_j B_{ij} \ln B_{ij}}{x_j + x_i B_{ij}} \right) \right), \quad (1)
$$

where R is the universal gas constant, T is the temperature of the mixture, x_i and x_j are the molar fractions of i and j, B_{ji} and B_{ij} are the pair-potential energy interaction parameters, which are defined as

$$
B_{ij} = \exp\left(-\frac{\varepsilon_{ij} - \varepsilon_{ii}}{kT} \right), \quad (2)
$$

where k is the Boltzmann constant and ε_{ij} is the pair potential energy of a central j atom and its first nearest neighbor i.

Moreover, the activity of the components i and j can be expressed as

$$
\ln \alpha_i = \ln \frac{x_i V_{\mathrm{m}i}}{x_i V_{\mathrm{m}i} + x_j V_{\mathrm{m}j} B_{ji}} +
$$
$$
+ x_j \left(\frac{V_{\mathrm{m}j} B_{ji}}{x_i V_{\mathrm{m}i} + x_j V_{\mathrm{m}j} B_{ji}} - \frac{V_{\mathrm{m}i} B_{ij}}{x_j V_{\mathrm{m}j} + x_i V_{\mathrm{m}i} B_{ij}} \right) -
$$
$$
- \frac{x_j^2}{2} \left(\frac{Z_i B_{ji}^2 \ln B_{ji}}{(x_i + x_j B_{ji})^2} + \frac{Z_j B_{ij} \ln B_{ij}}{(x_j + x_i B_{ij})^2} \right), \quad (3)
$$

$$
\ln \alpha_j = \ln \frac{x_j V_{\mathrm{m}j}}{x_j V_{\mathrm{m}j} + x_i V_{\mathrm{m}i} B_{ij}} -
$$
$$
- x_i \left(\frac{V_{\mathrm{m}j} B_{ji}}{x_i V_{\mathrm{m}i} + x_j V_{\mathrm{m}j} B_{ji}} - \frac{V_{\mathrm{m}i} B_{ij}}{x_j V_{\mathrm{m}j} + x_i V_{\mathrm{m}i} B_{ij}} \right) -
$$
$$
- \frac{x_i^2}{2} \left(\frac{Z_j B_{ij}^2 \ln B_{ij}}{(x_j + x_i B_{ij})^2} + \frac{Z_i B_{ji} \ln B_{ji}}{(x_i + x_j B_{ji})^2} \right). \quad (4)
$$

To determine the value of B_{ji} and B_{ij}, the activity of i in binary alloy, α_i, was fitted with Eq. (3) at a given temperature. The values of the physical parameters, V_{m} and Z, for the metals of interest in this work are taken from references [19] and [20]. The experimental activities were obtained by emf measurements in reference [21]. The final values of B_{ji} and B_{ij} are determined by minimizing the error $err = \sum_{i=1}^{n} |\alpha_{i,\exp} - \alpha_{i,\mathrm{MIVM}}|/n$, where n is the number of experimental data points, as far as possible by adjusting B_{ji} and B_{ij}.

The standard thermodynamic relation for the free energy of mixing (G) is

$$
G = G^{\mathrm{E}} + G^{\mathrm{id}} \quad (5)
$$

with

$$
G^{\mathrm{id}} = RT \left(x_i \ln x_i + x_j \ln x_j \right), \quad (6)
$$

where G^{id} is the molar ideal Gibbs energy.

2.2. Concentration fluctuation

The concentration fluctuation at the long wavelength limit $S_{xx}(0)$ is used to assess the response of demixing or ordering tendencies in the liquid alloy. It could serve as a sensitive test data of statistical models of liquid alloys, which can be easily obtained from standard relationship in terms of the free energy of mixing or in terms of activity, α_i, as:

$$
S_{xx}(0) = RT \left(\frac{\partial^2 G}{\partial x_i^2} \right)^{-1} = RT \left(\frac{\partial^2 G}{\partial x_j^2} \right)^{-1} =
$$
$$
= \alpha_i (1 - x_i) \left(\frac{\partial \alpha_i}{\partial x_i} \right)^{-1} = \alpha_j (1 - x_j) \left(\frac{\partial \alpha_j}{\partial x_j} \right)^{-1}. \quad (7)
$$

Using Eqs. (5) and (7), an expression to calculate $S_{xx}(0)$ is given by:

$$
S_{xx}(0) = \frac{x_i x_j}{1 + x_i f(x_i, x_j)}, \quad (8)
$$

where

$$
f(x_i, x_j) = \frac{V_{\mathrm{m}j} B_{ji} - V_{\mathrm{m}i}}{x_i V_{\mathrm{m}i} + x_j V_{\mathrm{m}j} B_{ji}} -
$$
$$
- \frac{V_{\mathrm{m}i} V_{\mathrm{m}j} B_{ji}}{(x_i V_{\mathrm{m}i} + x_j V_{\mathrm{m}j} B_{ji})^2} + \frac{V_{\mathrm{m}i}^2 B_{ij}^2}{(x_j V_{\mathrm{m}j} + x_i V_{\mathrm{m}i} B_{ij})^2} +
$$
$$
+ x_j \left(\frac{Z_i B_{ji}^2 \ln B_{ji}}{(x_i + x_j B_{ji})^3} + \frac{Z_j B_{ij}^2 \ln B_{ij}}{(x_j + x_i B_{ij})^3} \right) \quad (9)
$$

and for ideal mixing the molar excess Gibbs energy G^{E} given in Eq. (5) is equal to zero, and Eq. (8) reduces to

$$
S_{xx}^{\mathrm{id}}(0) = x_i x_j. \quad (10)
$$

2.3. Diffusivity

The mixing behavior of two atomic species of a binary liquid alloy is required for a proper understanding of the dynamical properties such as diffusion at the microscopic level. Based on Darken's thermodynamic equation, the relation between diffusion and $S_{xx}(0)$ can be written as:

$$\frac{D}{D_{id}} = \frac{S_{xx}^{id}(0)}{S_{xx}(0)}, \tag{11}$$

where D is the mutual diffusion coefficient and D_{id} is the intrinsic diffusion coefficient for the ideal mixture. The ratio D/D_{id} indicates the mixing nature of molten alloys: $D/D_{id} < 1$ indicates the tendency of homocoordination while $D/D_{id} > 1$ indicates the tendency of hetero-coordination and D/D_{id} approaches 1 for ideal mixing.

3. Results and discussion

3.1. Thermodynamic properties

The activity is an important thermodynamic quantity which is a measure of the minimum Gibbs energy needed to convert Zn atom from its state in the Zn-Bi solution to the pure state in any proposed extraction or refining process [18]. The experimental activities of zinc of Zn-Bi liquid alloy were taken from the electromotive force study of Hayer et al. [21]. The theoretical model described in the preceding section has been used to study the concentration dependence of some thermodynamic quantities of Zn-Bi binary liquid alloys at different temperatures. The values of B_{ji} and B_{ij} were determined by the overall fit of the experimental activity at different temperatures of the investigation, as given in Table 1. It can be observed that the parameters reproduced fairly well the experimental values of activity and free energy of mixing at the indicated temperatures (Figs. 1 and 2). Djaballah et al. calculated the Gibbs energy of the liquid phase of the Zn-Bi alloy by using the Redlich-Kister model, considering the dependence of enthalpy and entropy of mixing of the liquid on the temperature [22]. Their results were compared with known experimental and our calculated results, as shown in Fig. 2. This good agreement between calculated and experimental values of these thermodynamic quantities justifies the use of this model for this study.

In Fig. 1, we observed that α_{Zn} increases as x_{Zn} increases at each of the temperatures. However, if each of the α_{Zn} isotherms is closely compared with others, we found that:

1. The positive departure from ideality of the activity values decreases with increasing temperature.

Table 1. The values of B_{ji} and B_{ij} of Zn-Bi alloy at different temperatures

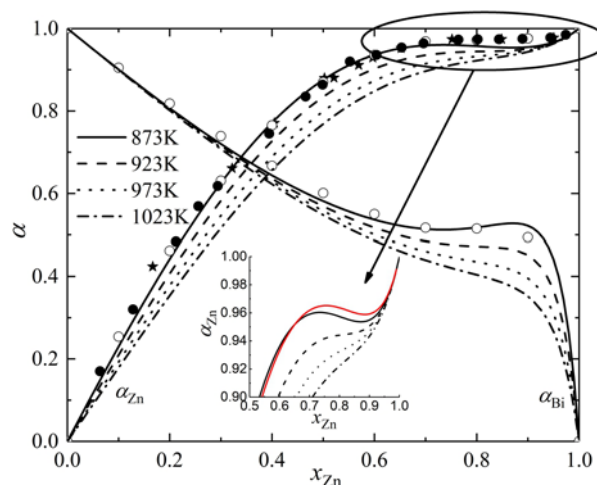| T (K)	B_{ji}	B_{ij}
873	1.1082	0.4456
923	1.1234	0.4538
973	1.1372	0.4612
1023	1.1500	0.4676

Fig. 1. Activity coefficients of (α_{Zn} and α_{Bi}) in Zn-Bi liquid alloys computed via Eqs. (3) and (4) at different temperatures, respectively. x_{Zn} is the concentration of Zn in the liquid alloys. The open circles [28], bullets [21], and pentagrams [29] are the experimental data at 873 K. The solid red line in the inset was calculated from the self-association model for $\gamma = 2.874$ and $W/RT = 1.326$ at 873 K.

2. Throughout the entire composition of Zn in the alloy, α_{Zn} at 1023 K is lower than at 873, 923, and 973 K.

3. The activity at 873 K has the maximum and minimum value at $x_{Zn} = 0.73$ and $x_{Zn} = 0.87$, respectively, as shown in the inset of Fig. 1. However, there is no extremum at 923, 973, and 1023 K. The activity at 873 K was also calculated from the self-association model, which was proposed by Singh and Sommer [3], for $\gamma = 2.874$ and $W/RT = 1.326$. The extrema also appear at $x_{Zn} = 0.76$ and $x_{Zn} = 0.88$, respectively, as shown in Fig. 1. Similarly, the extremum is non-existent at 923, 973, and 1023 K when the experimental activities were fitted by the self-association model.

Generally speaking, $\left|\frac{G}{RT}\right|$ increases as temperature increases at all concentrations, as shown in Fig. 2, which indicates that an increase in temperature enhances the atomic interactions in Zn-Bi system. Moreover, the free energy of mixing is always asymmetric from 873 to 1023 K. The position of the minimum
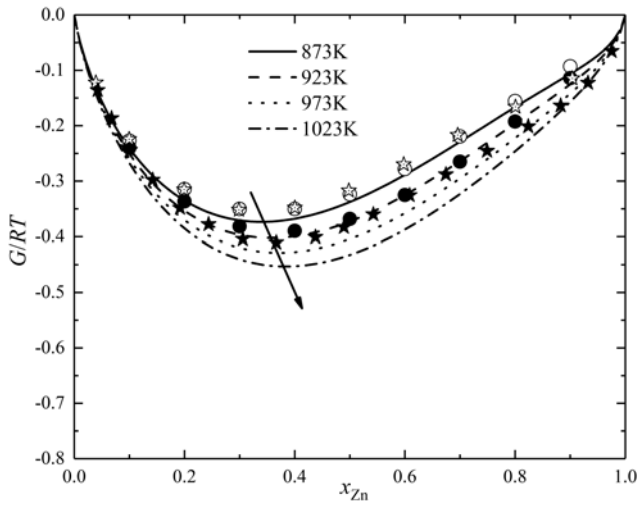
Fig. 2. Free energy of mixing: G/RT versus x_{Zn} for Zn-Bi liquid alloys at different temperatures, respectively. The open circles [28] and solid circles [21] are the experimental data at 873 K and 923 K, respectively. The open pentagrams [28] and solid pentagrams [21] are the experimental data at 873 and 973 K, respectively.

Fig. 3. $S_{xx}(0)$ in liquid Bi-Zn alloys at different temperatures. The square is the experimental data at 873 K [8].

value of G/RT shifts to $x_{Zn} = 0.50$ with increasing temperature, as shown by the arrow in Fig. 2, which suggests that the degree of segregation is weakened and the local order in the Zn-Bi alloy moves to the hetero-coordination of unlike atoms as the temperature is increased considerably. In this range of composition, the temperature increase from 873 to 1023 K led to as much as 17.6 % increase in $\left|\frac{G}{RT}\right|$. That at all temperatures the value of $\left|\frac{G}{RT}\right|$ is far less than 3.0, is an indication that the energy of complex formation in Zn-Bi liquid alloys is small and hence, Zn-Bi liquid alloys are weakly interacting systems. Also, the asymmetric behavior relates to equiatomic composition typical of systems with atomic volume ratio $\frac{V_{m,Bi}}{V_{m,Zn}} > 2.0$ [23] which in the present study is about 2.12 for Zn-Bi liquid alloy.

3.2. Concentration fluctuation

To understand the nature, strength, and level of influence of the order in the properties of the alloys, we consider the calculated $S_{xx}(0)$ using Eq. (8). Figure 3 shows a plot of $S_{xx}(0)$ against concentrations of zinc. The calculated values of $S_{xx}(0)$ are in agreement with the experimental values of $S_{xx}(0)$. The result can be used to understand the nature of atomic order in binary liquid alloys. Essentially, $S_{xx}(0) > S_{xx}^{id}(0)$ indicates the tendency of segregation in the liquid alloy. A perusal of Fig. 3 shows the demixing tendencies in Zn-Bi liquid alloy at all the temperatures albeit at varying degrees. This is an indication that Zn-Bi liquid alloys are homocoordinated and that the homocoordination
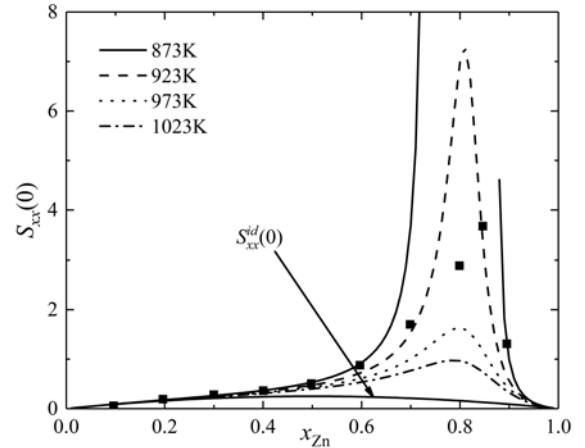
which is strong is indicated by the relatively high peak at various temperatures when compared with weakly homocoordinated alloys like Zn*Cd liquid alloys [24]. It should be noticed that there is a relatively large reduction in the peak value of $S_{xx}(0)$ as the temperature increased from 923 to 1023 K. This trend in the reduction of the peak value of $S_{xx}(0)$ suggests some form of the reduction in the demixing tendencies of this alloy with an increase in temperature. This trend also suggests that with further increase in temperature, the $S_{xx}(0)$ of the alloy approaches ideal values. The reduction in the demixing tendencies of Zn-Bi liquid alloy can be associated with the dissociation of the segregating clusters of the liquid alloy components. This dissociation of clusters occurs as a result of the increase in the temperature of the alloy.

3.3. Diffusion

It has been reported that transport properties such as diffusivities of metals in the liquid state are needed for many metallurgical processes [24]. Also, from the practical point of view, the viscosity is reported to be one of the key parameters for the design and optimization of metallurgical processes [25]. Gruner et al. in [26] reported that a study of the viscosity of liquid alloys contributes to the understanding of the relations between atomic structure and physical properties of alloys since properties like viscosity and diffusion are strongly sensitive to structural changes concerning temperature and composition. Hence, we have extended our investigation of the effects of temperature on the properties of Zn-Bi liquid alloys, to investigate effects of temperature on its diffusivity properties, using Eq. (11). The results obtained are shown in Fig. 4. Although, in these figures due to the lack of experimental data, it is not possible to compare
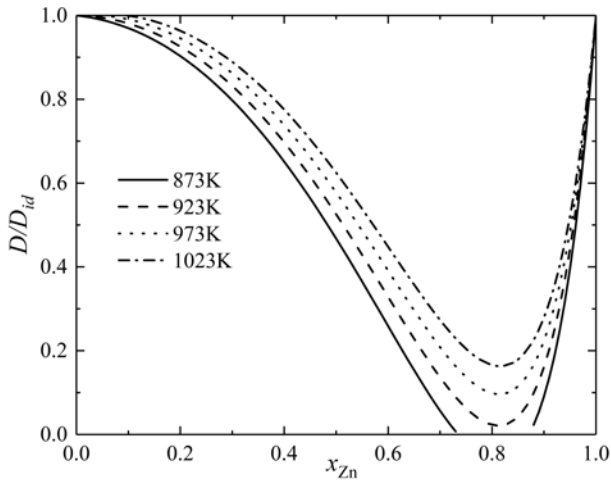
Fig. 4. Diffusion coefficients, D/D_{id}, of liquid Bi-Zn alloys at different temperatures.

computed and experimental results. Thus, these agreements serve as an evidence of the reliability of the following observations in Fig. 4:

1. At all temperatures, the magnitude of diffusivity reduces from unity towards minimum and then increases towards unity as the composition of Zn in the alloy increases;

2. The magnitude of the minimum diffusivity increases as the temperature increases;

3. Change in temperature resulted in increasing 6.74 fold in the magnitude of the diffusivity of Zn-Bi liquid alloys (i.e., when $x_{Zn} = 0.81$, diffusivity = 0.0211 at 923 K, while diffusivity = 0.1633 at 1023 K).

In our analysis, the quantity of central importance is $S_{xx}(0)$ which is strongly concentration and temperature dependent for demixing liquid alloys. It is the temperature dependence of $S_{xx}(0)$ which allows us to investigate the temperature dependence of D. To exhibit the temperature dependence of diffusion coefficients, $\ln(D/D_{id})$ and D/D_{id} computed from Eq. (11) for the compositions $Zn_{0.95}Bi_{0.05}$, $Zn_{0.70}Bi_{0.30}$ and $Zn_{0.30}Bi_{0.70}$ are plotted in Fig. 5 as a function of $1/T$. The results clearly suggest that $\ln(D/D_{id})$ at $x_{Zn} = 0.7$, in the vicinity of the critical components is obviously in disagreement with the Arrhenius type of temperature dependence. However, far away from the critical composition, it displays a straight line behavior, i.e., at $x_{Zn} = 0.3$ and $x_{Zn} = 0.95$. It should be noted that D/D_{id} for all the compositions depends linearly on $1/T$, which is in agreement with the observations of Singh [27].

4. Conclusions

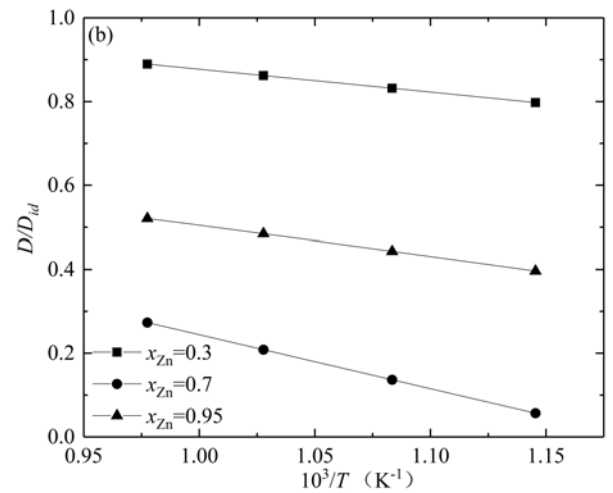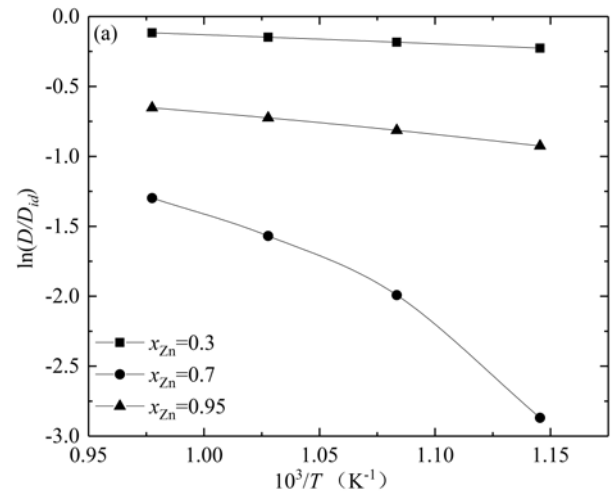Molecular interaction volume model (MIVM) has been used to predict the thermodynamic activities of

Fig. 5. Diffusion coefficients against temperature for the liquid $Zn_{0.95}Bi_{0.05}$, $Zn_{0.70}Bi_{0.30}$, $Zn_{0.30}Bi_{0.70}$, respectively: (a) ($\ln(D/D_{id})$ against T^{-1}) and (b) (D/D_{id} against T^{-1}).

all components in the liquid Zn-Bi system in the temperature range 873–1023 K. The results of our calculations reveal the following:

1. The calculated values of activity and free energy of mixing agree well with the experimental values at 873, 923, 973, and 1023 K.

2. The calculated concentration fluctuation $S_{xx}(0)$ indicated the strong tendency of segregation in liquid Zn-Bi alloys. With the temperature increasing, the homocoordinated clusters dissociated and the liquid alloy approached the ideal state.

3. The diffusivity properties increased quickly with the temperature increasing. $\ln(D/D_{id})$ in the vicinity of the critical components is obviously in disagreement with the Arrhenius type of temperature dependence, while far away from the critical composition it displays a straight line behavior with $1/T$. Moreover, D/D_{id} depends linearly on $1/T$ for all the compositions.

The results obtained in this paper serve as the contribution to a complete thermodynamic description of Zn-Bi system. The results also confirm that MIVM is a reliable model for predicting the thermodynamic activities of liquid binary alloys.

Acknowledgements

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