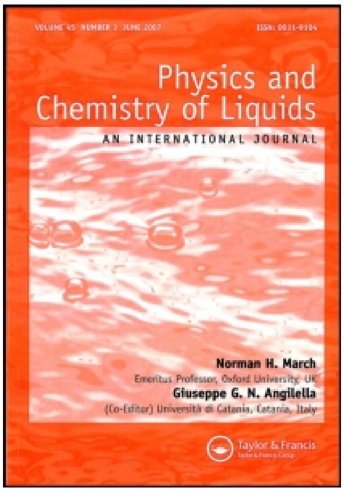

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Thermodynamic evaluation of viscosity in In–Zn and Sn–Zn liquid alloys

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A theoretical formalism that links thermodynamic properties to transport properties has been used to study the viscosity of Sn–Zn and In–Zn liquid alloys at various temperatures. The formalism was successful at describing the thermodynamic properties of these alloys and showed a better estimation of the viscosity of the Sn–Zn alloy than that of the In–Zn alloy.

Keywords: Liquid alloys; Phase-segregation; Viscosity

1. Introduction

The understanding of the statics and dynamics of metallic liquid alloys has become a subject of study in recent times. These studies include the investigation of the structural, thermodynamic and transport properties of the alloys. Many measurements have been made on the thermodynamic properties of liquid binary alloys [1] and some measurements on the transport properties of some metals and alloys [2]. However, very little investigation has been made on the relationship between thermodynamic properties and transport properties. Neale and Cusack [3] attempted an investigation with a view to obtaining a comprehensive empirical description between thermodynamic and transport properties in Na–Cs liquid alloys. A theoretical attempt to link thermodynamic properties of liquid binary alloys to some transport properties has been made by Singh and Sommer [4]. In their work they presented a simple formalism which relates viscosity and diffusion coefficient to the thermodynamic properties of metallic alloys. This kind of formalism if it is in reasonable agreement with experimental measurements could serve as a unique economic and effective method to predict the properties of liquid metallic binary alloys, depending less on experimental data.

Some authors have worked on this formalism and applied it in calculating the viscosity of liquid Cu–Bi and Bi–Zn alloys [5] and liquid Na–K and Na–Cs alloys [6]

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by using energetics determined from thermodynamic data. The results appear impressive as it showed that for alloys with large size difference, the predictive power of the model is decreased towards some concentration range, and for alloys with size ratio close to one, the calculated viscosity values are reasonably close to the measured and estimated values of viscosity.

In this article, the predictive power of the formalism at different temperature is investigated for the Sn–Zn and In–Zn liquid alloys. These alloys are considered as possible candidates to replace the common Sn–Pb solders [7]. In addition to the properties such as liquidus temperature, pasty range, wettability, microstructure, mechanical properties as well as reliability of soldered joints, it is clear that other factors of interest to be considered for a good soldering candidate material include interfacial adhesion, surface tension and viscosity as they play an important role in producing acceptable solder joints [8,9]. Hence, the ability of this formalism in describing the transport properties of this class of liquid alloys will be of interest.

2. Theory

Singh and Sommer [4] showed that there exists a relation between viscosity and diffusion coefficient D_m for a liquid A–B alloy. The relation they obtained is

$$\eta = \frac{k_{\mathrm{B}}T}{D_m}\left(\frac{c_A}{\sigma_B} + \frac{c_B}{\sigma_A}\right)\phi \tag{1}$$

$$= \eta_0\phi \tag{2}$$

where

$$\eta_0 = \frac{k_{\mathrm{B}}T}{D_m}\left(\frac{c_A}{\sigma_B} + \frac{c_B}{\sigma_A}\right) \tag{3}$$

c_A and c_B are the concentrations of the A and B components of the alloy, $\sigma_i, (i = A, B)$ depends on the size and shape of the diffusing particles. η is the coefficient of viscosity and the factor ϕ is related to concentration fluctuation in the long wavelength limit $S_{cc}(0)$ as:

$$\phi = \frac{c_A c_B}{S_{cc}(0)} \tag{4}$$

Ideally, η_0 is expected to be linear in c and experimental results have shown this [4]. Consequently, the observed deviations in the $\eta - c$ isotherm occur as a result of the factor ϕ. This factor was investigated by Osman and Singh [11]. They obtained a general relation for the dependence of ϕ on the enthalpic (W) and entropic (γ) effects as

$$\phi = 1 - c_A c_B g(\gamma, W) \tag{5}$$

with

$$g(\gamma, W) = \frac{2\gamma^2 W - (\gamma - 1)^2 (c_A + \gamma c_B)}{(c_A + \gamma c_B)^3} \tag{6}$$

$$W = \Omega_A \left(\frac{\omega}{k_\mathrm{B} T} \right) \tag{7}$$

where ω is the interchange energy given as:

$$\omega = \left(\varepsilon_{AB} - \frac{\varepsilon_{AA} + \varepsilon_{BB}}{2} \right) \tag{8}$$

ε_{ij} are i–j bond strengths and γ ($\equiv \Omega_B/\Omega_A; \Omega_A < \Omega_B$) is the size ratio.

With equations (2), (5)–(7) one has

$$\frac{\Delta\eta}{\eta_0} = -c_A c_B g(\gamma, W) \tag{9}$$

where $g(\gamma, W)$ embodies the energetics and the size effects responsible for the characteristic behaviour of $\Delta\eta$ for a given binary alloy.

Taking into account the enthalpic effect only in equation (9) and using conformal solution results, one relates $\Delta\eta/\eta_0$ to enthalpy of formation (H_M) [4] as

$$\frac{\Delta\eta}{\eta_0} = -\frac{H_M}{RT} \tag{10}$$

where R is the ideal gas constant.

To relate thermodynamic quantities to viscosity coefficient (η), one uses free energy of mixing (G_M) which incorporates the size effects. This equation is given as

$$G_\mathrm{M} = N k_\mathrm{B} T \left(c_B \ln \psi + c_A \ln(1 - \psi) + c_A \psi W \right) \tag{11}$$

k_B is the Boltzman constant and ψ is the concentration by atomic volume species given by

$$\psi = \frac{\gamma c_B}{c_A + \gamma c_B} \tag{12}$$

3. Results and discussion

Ordinarily, the parameter γ is determined from experimental density measurements. Since such data were not available, γ was treated as a free parameter along with W. Thus, the values of γ and W were chosen to reproduce simultaneously an overall fit of the concentration fluctuation in the long wavelength limit ($S_{cc}(0)$) and free energy of mixing (G_M/RT). The experimental values of concentration fluctuation in the long wavelength limit ($S_{cc}(0)$) used in this work were derived from the activity data of Sn–Zn and In–Zn given in [12–17], and they were also used by Lee [10]. The quantity $S_{cc}(0)$ was derived from the relation

$$S_{cc}(0) = c_i a_j \left(\frac{\partial a_j}{\partial c_j} \right)^{-1}_{T,P}$$

where c_i and a_j are the concentration and activity of component i, $j\,(i, j = A, B)$, respectively.

The experimental and fitted values of $S_{cc}(0)$ for the two alloys, Sn–Zn and In–Zn, at different temperatures are shown in figures 1(a) and 1(b). The experimental values

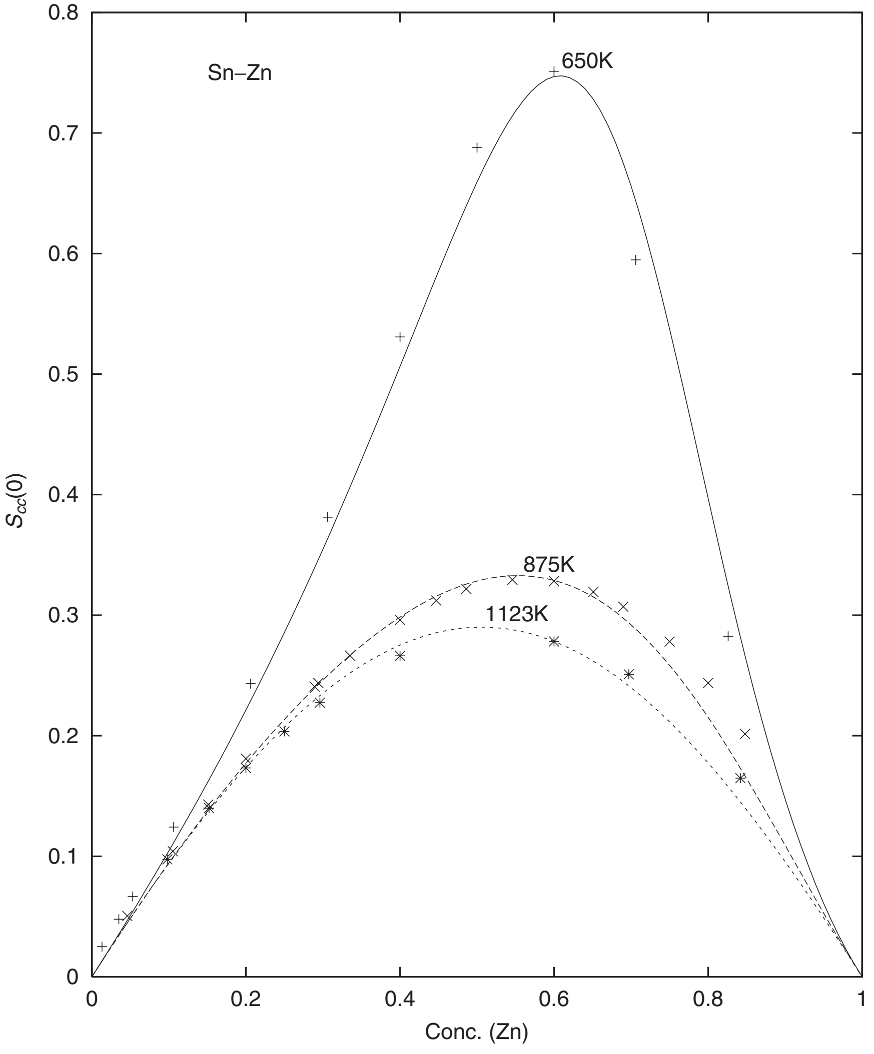

Figure 1. $S_{cc}(0)$ *versus* concentration of Zn (a) for Sn–Zn liquid alloy (b) for In–Zn liquid alloy. Lines represent calculated values, points represent experimental values at the temperature indicated.

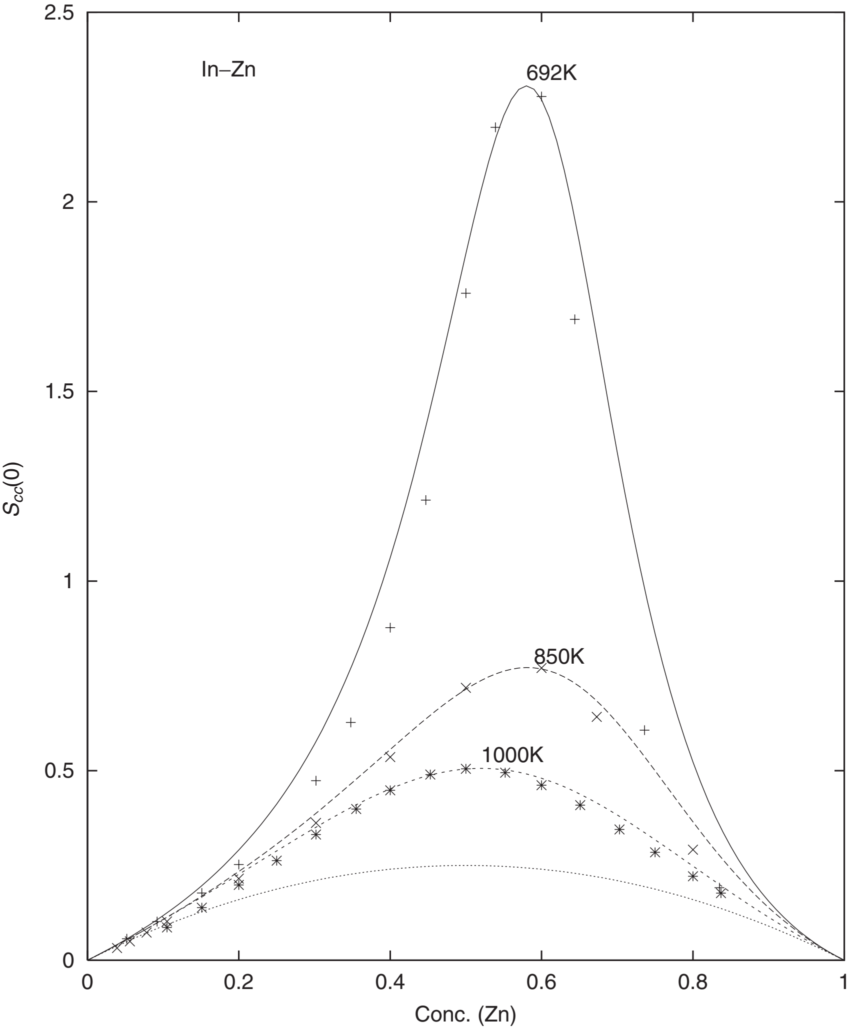

Figure 1. Continued.

of Sn–Zn alloy at 650 K, 875 K and 1123 K are due to Hamaguchi and Asano [12], Ptak [13] and Kozuka and Moriyama [14], respectively. For In–Zn alloy, the experimental values are due to Oelsen and Zühlke [15], Moser [16] and Hagiwara *et al.* [17] at temperature values of 692 K, 850 K and 1000 K, respectively. The values of γ and W used in fitting these curves are shown in table 1. But for the slight deviations between 0.75 and 0.84 atomic concentration of Sn–Zn at 875 K, the predictive power of the model was decreased for a highly phase-segregating alloy as depicted by In–Zn. For Sn–Zn alloy that has relatively low segregating tendencies, it had better estimation, predicting the rapid change seen in Sn–Zn from phase-segregating liquid to regular liquid alloy in accordance with experiment.

Figures 2(a) and 2(b) show the calculations performed for free energy of mixing for both alloys. These show that the calculations compared favourably well with the

Table 1. The values of size ratio (γ) and order energy (W) used to fit the thermodynamic properties.

Alloy at a given temp.	Size ratio (γ)	Order energy (W)
Sn–Zn (650 K)	1.523	1.149
Sn–Zn (875 K)	1.657	0.512
Sn–Zn (1123 K)	1.126	0.268
In–Zn (692 K)	1.272	1.595
In–Zn (850 K)	1.392	1.196
In–Zn (1000 K)	1.112	0.966

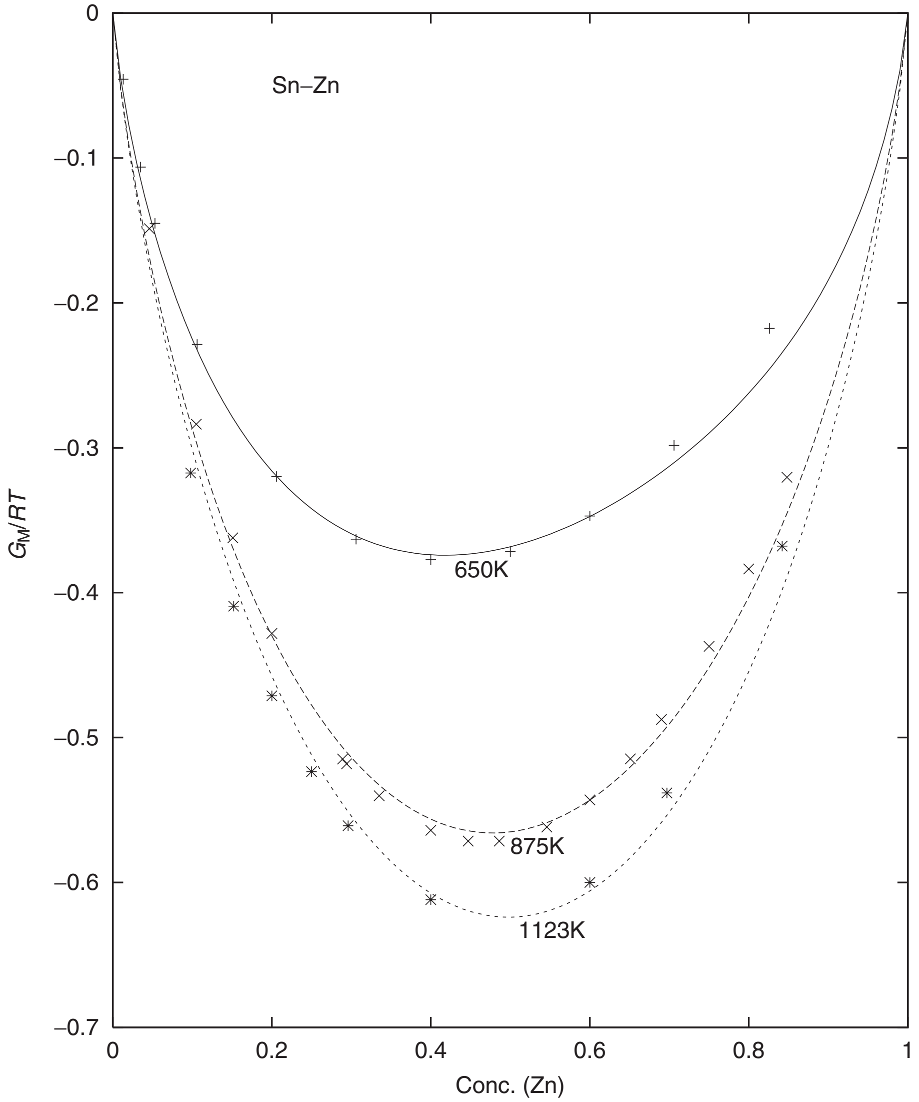

Figure 2. G_M/RT *versus* the concentration of Zn (a) for Sn–Zn liquid alloy (b) for In–Zn liquid alloy. Lines represent calculated values while points represent the experimental values at the temperature indicated.

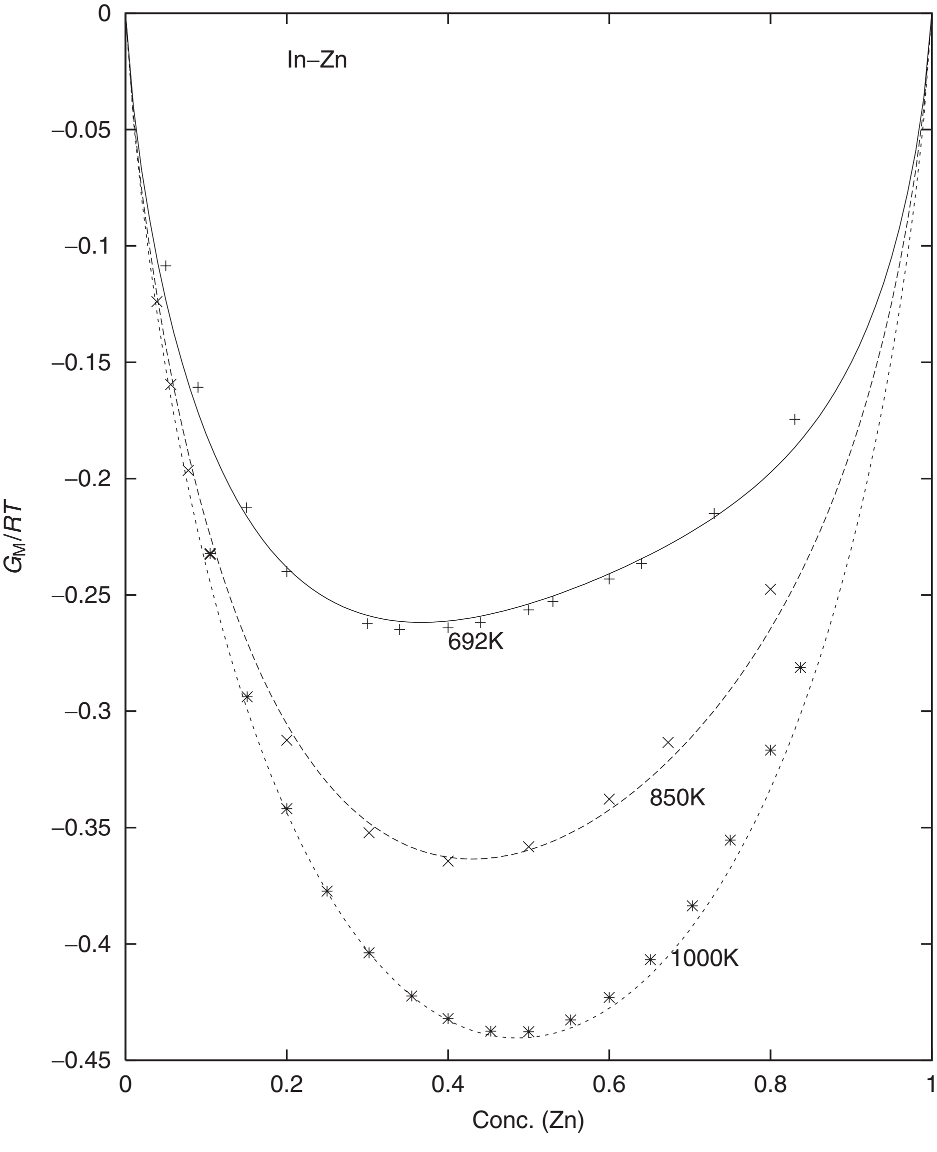

Figure 2. Continued.

experiment at all temperatures, predicting the observed decrease in free energy of mixing with increasing temperature values in accordance with the experimental results.

Figures 3(a) and 3(b) show the calculated $\Delta\eta/\eta_0$ values for Sn–Zn and In–Zn, respectively. There are no experimental viscosity values available to the authors at the time of writing. However, experimental $\Delta\eta/\eta_0$ values used were calculated from experimental enthalpy values using equation (10). For Sn–Zn alloy, $\Delta\eta/\eta_0$ values were calculated at temperatures of 650 K, 875 K and 1123 K while for In–Zn these values were calculated at temperatures of 692 K, 850 K and 1000 K. Since there were no enthalpy values at these temperatures for both alloy systems, viscosity

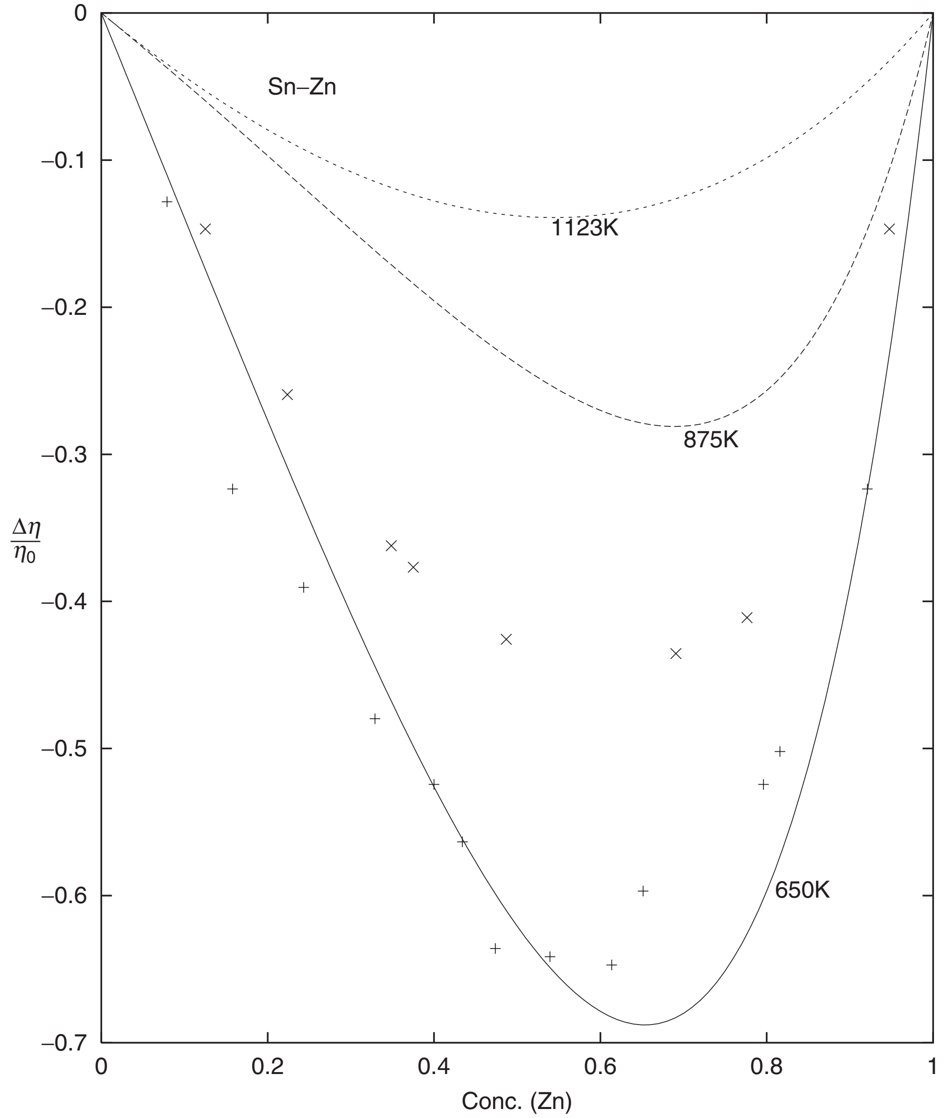

Figure 3(a). $\Delta\eta/\eta_0$ *versus* concentration of Zn for Sn–Zn liquid alloy. Lines are calculated values at their indicated temperature. (+++) are estimated values at 700 K [18], (×××) are estimated values at 798 K [19].

values were estimated from enthalpy values at 700 K and 798 K for Sn–Zn alloy and at 700 K and 733 K for In–Zn alloy. The enthalpy values of Sn–Zn alloy at 700 K and 798 K were due to Moser *et al.* [18] and Kleppa [19], respectively. While those for In–Zn alloy at 700 K and 733 K were due to Svirbely and Selis [20], and Wittig and Müller [21], respectively.

For Sn–Zn alloy, the graphs show that the calculated values of $\Delta\eta/\eta_0$ appear to give a close estimate of the measured values. In general, the graphs show that the viscosity coefficient increases with increasing temperature for all concentrations. The figure for In–Zn shows that the formalism gives poor prediction for the measured $\Delta\eta/\eta_0$

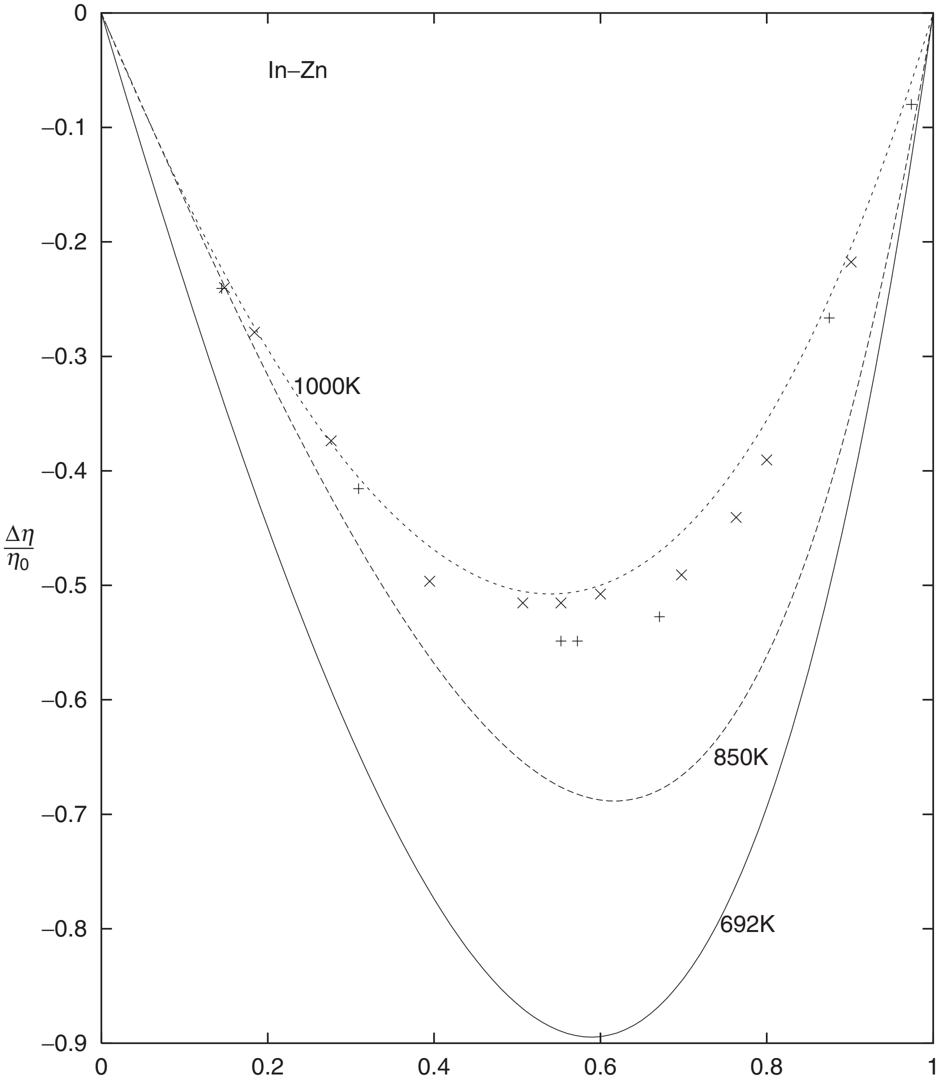

Figure 3(b). $\Delta\eta/\eta_0$ *versus* concentration of Zn for In–Zn liquid alloy. Lines are calculated values at their indicated temperature. (×××) are estimated values at 700 K [20], (+++) are estimated values at 733 K [21].

values. In–Zn alloy has a higher phase-segregating tendency than Sn–Zn as can be observed from their $S_{cc}(0)$. This poor prediction of viscosity values of In–Zn alloy is in agreement with the behaviour of Bi–Zn alloy whose peak value of $S_{cc}(0)$ is about 4.0 as shown in the work of Akinlade *et al.* [5]. In their work, calculated $\Delta\eta/\eta_0$ for Bi–Zn showed large over-prediction of the experimental values, while Cu–Bi with lesser phase-segregating tendency as in Sn–Zn had better agreement with the estimated values of $\Delta\eta/\eta_0$. We therefore infer that this formalism is poor at predicting the viscosity values for strongly phase-segregating binary alloy systems especially for binary liquid alloy systems whose peak value of $S_{cc}(0)$ is reasonably greater than 1.0.

4. Conclusion

The formalism due to Singh and Sommer usefully describes the thermodynamic properties of Sn–Zn and In–Zn liquid alloys. However, its ability to determine the $\Delta\eta/\eta_0$ values appears better for the Sn–Zn alloy than for the In–Zn alloy. The formalism may need refinement for strongly phase-segregating alloys whose peak values of $S_{cc}(0)$ are appreciably greater than 1.0.

References

[1] R.N. Singh, F. Sommer. *Rep. Prog. Phys.*, **60**, 50 (1997).
[2] T. Iida, R.I.L. Guthrie. *The Physical Properties of Liquid Metals*, Clarendon Press, Oxford (1988).
[3] F.E. Neale, N.E. Cusack. *J. Phys. F: Met. Phys.*, **12**, 2839 (1982).
[4] R.N. Singh, F. Sommer. *Phys. Chem. Liq.*, **36**, 17 (1998).
[5] O. Akinlade, R.N. Singh, F. Sommer. *J. Alloys. Compds.*, **267**, 195 (1998).
[6] B.C. Anusionwu. *Indian J. Phys.*, **78**, 1269 (2004).
[7] Y.-S. Kim, K.-S. Kim, C.-W. Hwang, K Suganuma. *J. Alloys. Compds.*, **352**, 237 (2003).
[8] R.R. Kapor, T.W. Eagar. *Metall. Trans.*, **20**, 919 (1989).
[9] C.J. Thwaites. *Int. Mater. Rev.*, **29**, 45 (1984).
[10] B.-J. Lee. *Calphad*, **20**(4), 471 (1996).
[11] S.M. Osman, R.N. Singh. *Phy. Rev.*, **E51**, 332 (1995).
[12] M. Hamaguchi, N. Asano. *Mem. Ehi. Univ.*, *Sect. III Eng.*, **7**, 51 (1973).
[13] W. Ptak. *Arch. Hutnictwa*, **5**, 169 (1960).
[14] Z. Kozuka, J. Moriyama. *Suiyokwai-Shi*, **16**, 163 (1967).
[15] W. Oelsen, P. Zühlke. *Arch. Eisenhüttenwes.*, **27**, 743 (1956).
[16] Z. Moser. *Rev. Rom. Chim.*, **16**, 327 (1971).
[17] H. Hagiwara, S. Sugino, H. Fujiwara. *Bull. Univ. Osaka*, **23**, 41 (1974).
[18] Z. Moser, K. Rzyman, S. Randzio. *Bull. Pol. Acad. Sci.*, *Tech. Sci.*, **35**, 461 (1987).
[19] O.J. Kleppa. *J. Phys. Chem.*, **59**, 354 (1955).
[20] W.J. Svirbely, S.M. Selis. *J. Am. Chem. Soc.*, **75**, 1532 (1953).
[21] F.E. Wittig, E. Müller. *Z. Metallkd.*, **51**, 226 (1960).