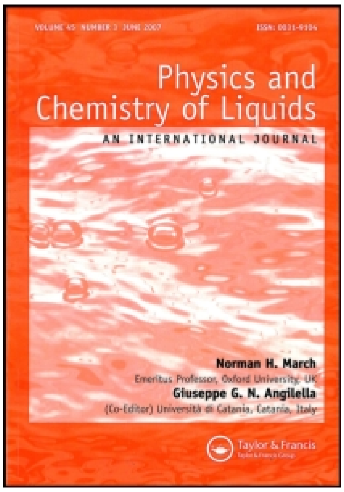

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Thermodynamic studies of the surface and transport properties in Ag-In and Ag-Sb liquid alloys

B. C. Anusionwu[a][b]; O. K. Echendu[a]
[a] Department of Physics, Federal University of Technology, Owerri, Nigeria [b] Abdus Salam International Center for Theoretical Physics, Trieste, Italy

To cite this Article Anusionwu, B. C. and Echendu, O. K.(2010) 'Thermodynamic studies of the surface and transport properties in Ag-In and Ag-Sb liquid alloys', Physics and Chemistry of Liquids, 48: 1, 127 — 140
To link to this Article: DOI: 10.1080/00319100902774128
URL: http://dx.doi.org/10.1080/00319100902774128

Physics and Chemistry of Liquids
Vol. 48, No. 1, February 2010, 127–140

Thermodynamic studies of the surface and transport properties in Ag–In and Ag–Sb liquid alloys

B.C. Anusionwu[ab]* and O.K. Echendu[a]

[a]*Department of Physics, Federal University of Technology, Owerri, Nigeria;* [b]*Abdus Salam International Center for Theoretical Physics, Trieste, Italy*

(*Received 24 September 2008; final version received 24 January 2009*)

The surface tension, surface concentration, viscosity and mutual diffusion co-efficients of the Ag–In and Ag–Sb liquid alloys have been calculated using energetics and derivables from a statistical mechanical framework which recognises the formation of atom clusters of self associates. Our calculations suggest the existence of some form of local order in the systems. Ag–In showed higher tendencies to heterocoordination in the bulk-manifested higher values of mutual diffusion coefficient throughout the concentration range. The viscosity values of Ag–In and Ag–Sb were calculated using the expression reported by Kucharsky which relates the viscosity of a liquid binary alloy to the activity coefficients of the liquid alloy components that are raised to some power m. This exponent m is a fitted parameter. The calculated viscosity values for Ag–Sb had some reasonable agreement with experiment above 0.5 atomic fraction of Sb, using a fitted parameter value of $m = 4.5$. The fitted parameter value for the viscosity of Ag–In is expected to be in the range $1.5 \leq m \leq 3.5$.

Keywords: diffusion co-efficients; viscosity; surface tension; liquid alloys

1. Introduction

The need to develop new lead-free solder materials as an alternative to lead solder due to environmental concerns has become of worldwide interest [1]. The development of such new materials sometimes requires the knowledge of thermodynamic and thermophysical data which due to experimental difficulties have not been measured [2]. Some of these properties whose data for alloys are scanty due to difficulties in measurement at high temperatures include transport properties such as viscosities and mutual diffusivities and also surface properties such as surface tension and surface concentration [3]. It is therefore necessary to estimate these sets of data using theoretical models. For this purpose, different theoretical models are available [3–7]. Some of these models require thermodynamic information such as interchange energy, activity co-efficient and the concentration fluctuation at the long wavelength limit for the estimation of the properties. This underlines the importance of thermodynamic studies for liquid binary alloys.

---

*Corresponding author. Email: abedec@yahoo.com

ISSN 0031–9104 print/ISSN 1029–0451 online

DOI: 10.1080/00319100902774128
http://www.informaworld.com

In the class of new alloys intended for use in different technological applications are the silver-based alloys. For instance, Ag–Ti, Ag–Zr and Ag–Hf alloys have been studied as active brazers with ceramic substrates in composite materials suitable for application where aggressive thermal and mechanical conditions are permanent [2]. The traditional silver solders have been used for joining ceramics and glasses with metallic materials [8]. Moreover, in the selection of multicomponent alloys for lead-free solders, the binary Ag–In system takes part as one of the possible binary contributions [1]. In view of the potentially useful technological applications of silver-based alloys [9], there is need for a good understanding of their thermodynamic and thermophysical properties.

The thermodynamic properties of Ag–In and Ag–Sb have been studied by many authors [10–15]. These studies used different experimental methods to determine the various thermodynamic quantities of these alloys, such as the activities and free energy of mixing. However, these studies do not provide information on the transport and surface properties of these alloys. In this study therefore, we use the emf measurements of Krzyak and Fitzner [16] for Ag–Sb, and Jendrzejezyk and Fitzner [1] for Ag–In to estimate the mutual diffusivities, viscosities and surface properties throughout the concentration range.

2. Theoretical models

2.1. *Thermodynamic properties*

The simple statistical model proposed by Singh and Sommer [17] assumes that a liquid binary A–B alloy consisting of N_A atoms of element A and N_B atoms of elements B situated at equivalent sites, having short-ranged interaction effective only between nearest neighbours forms a polyatomic matrix leading to the formation of like atom clusters or self associates of type μA and νB, where μ and ν are the number of atoms in the clusters of type A and B matrices, respectively.

The thermodynamic properties of this category of liquid alloys depends on the number of self associates, $n = \mu/\nu$. Using the quasi-chemical approximation, an expression for the Gibbs free energy is obtained as,

$$G_m = RT[c \ln c + (1-c)\ln(1-c) + c\ln(1-\xi) + \ln\Gamma] + c(1-c)\Gamma W, \tag{1}$$

where c is the concentration of atom A, $W = \mu w$, $\xi = 1 - 1/n$ and $\Gamma = 1/(1 - c\xi)$ and w is the interchange energy. The activities of the alloy components can be determined from the general expression,

$$RT \ln a_i = \left(\frac{\partial G_m}{\partial N_i}\right)_{T,p,N}. \tag{2}$$

Using Equation (1) in (2), expressions for activity (a_i) of the alloy components are obtained as

$$\ln a_A = \ln(c\Gamma(1-\xi)) + (1-c)\Gamma\xi + (1-c)^2\Gamma^2\frac{W}{RT}, \tag{3}$$

$$\ln a_B = \ln(c\Gamma) + c(1-\xi)\Gamma(1-n) + nc^2(1-\xi)\Gamma^2\frac{W}{RT}, \tag{4}$$

where R is the molar gas constant and the activity co-efficients (γ_i) can be obtained from the relation

$$\gamma_i = a_i/c_i. \tag{5}$$

The expression for the bulk concentration–concentration fluctuations at the long wavelength limit ($S_{cc}(0)$) is in general given as

$$S_{cc}(0) = RT\left(\frac{\partial^2 G_m}{\partial c^2}\right)^{-1}_{T,P,N}. \tag{6}$$

Under the present formulation, the $S_{cc}(0)$ is given by the expression

$$S_{cc}(0) = \frac{c(1-c)}{1 - c(1-c)g(n, W)}, \tag{7}$$

where

$$g(n, W) = \frac{2n^2(W/RT) - (n-1)^2[c + n(1-c)]}{[c + n(1-c)]^3}. \tag{8}$$

The Warren–Cowley short-range order parameter for the first nearest neighbours (α_1) is related to the $S_{cc}(0)$ according to the expression

$$\alpha_1 = \frac{(S-1)}{s(z-1)+1}, \tag{9}$$

where

$$S = \frac{S_{cc}(0)}{c(1-c)}, \tag{10}$$

and z is the coordination number.

2.2. *Diffusivity and viscosity*

Using the Darken's thermodynamic equation for diffusion [18], the concentration–concentration fluctuation at the long wavelength limit $S_{cc}(0)$ has been related to the diffusivities of the species of the liquid binary alloys via the relation [17,19]

$$\frac{D_M}{D_{id}} = \frac{S^{id}_{cc}(0)}{S_{cc}(0)}, \tag{11}$$

where D_M is the mutual diffusivities of the alloy, and D_{id} is the intrinsic diffusivities for an ideal mixture of liquid alloy components which can be obtained from

$$D_{id} = cD_B + (1-c)D_A, \tag{12}$$

where D_i are the self diffusivities of pure alloy components A and B, respectively. The mutual diffusivities for the alloy across the whole concentration range can be computed from Equation (11) if the self diffusivities D_i are known from the experiment. Since values of diffusivities of pure components of liquid alloys are scanty, they can be predicted, to a reasonable extent, using theoretical models. One such model is the one due to Protopapas *et al.* [4] for the determination of self diffusivities of liquid metals based on the hard sphere model. The expression for diffusivities is given as

$$D = \sigma C_{\mathrm{AW}}(\eta)\left(\frac{\pi RT}{M}\right)^{\frac{1}{2}}\frac{(1-\eta)^3}{8\eta(2-\eta)}, \tag{13}$$

where R, T and M are the universal gas constant, absolute temperature, and atomic weight respectively. The values of σ, η and $C_{AW}(\eta)$ can be calculated from the following expressions

$$\sigma = 1.126\sigma_m\left[1 - 0.112(T/T_m)^{\frac{1}{2}}\right], \tag{14}$$

where σ_m is the value of σ at the melting temperature T_m. Taking the packing fraction of the liquid metal at melting point η_m as 0.472, σ_m becomes

$$\sigma_m = 1.41(M/\pi\rho_m N_{\mathrm{A}})^{\frac{1}{2}}; \tag{15}$$

ρ_m is the atomic density at the melting point and N_{A} is the Avogadro's number, π retains its usual meaning. Then the packing fraction at any temperature T is given as

$$\eta = \frac{0.472\rho\sigma^3}{\rho_m\sigma_m^3}, \tag{16}$$

ρ is the atomic density at temperature T, ρ can be obtained from the expression $\rho = \rho_m + \Lambda(T - T_m)$ with $\Lambda = \partial\rho/\partial T$. Once the value of η is known, the correction factor $C_{AW}(\eta)$ known as the Alder–Wainwright correction is obtained from a chart [3,4].

The viscosity of a liquid binary alloy can be estimated using the expression reported by Kucharsky [20]. This expression relates the viscosity of a liquid binary alloy to the activity co-efficients of the liquid alloy components. The viscosity ξ of a liquid binary alloy is given as

$$\xi = c_A\frac{V_A}{V_{\mathrm{M}}}\left(\frac{v_A}{v}\right)^2\gamma_A^m\xi_A + c_B\frac{V_B}{V_{\mathrm{M}}}\left(\frac{v_B}{v}\right)^2\gamma_B^m\xi_B; \tag{17}$$

v_A, v_B and v are defined by the expressions

$$v_A = c_A V_A^{\frac{1}{3}} + \frac{c_B V_B^{\frac{4}{3}}}{V_A}, \tag{18}$$

$$v_B = c_B V_B^{\frac{1}{3}} + \frac{c_A V_A^{\frac{4}{3}}}{V_B}, \tag{19}$$

$$v = c_A V_A^{\frac{1}{3}} + C_B V_B^{\frac{1}{3}}. \tag{20}$$

In the above equations, m is a fitted parameter, V_{M} is the molar volume, V_A and V_B are the atomic volume of pure components A and B of the alloy, γ_A and γ_B are there respective activity co-efficients while ξ_A and ξ_B are their viscosities.

2.3. *Surface properties*

In the model for studying surface properties, a statistical mechanical approach which derives from the concept of a layered structure near the interface was used by Prasad *et al.* [21] to obtain expressions for surface properties. The surface grand partition function Ξ^s is related to the surface tension σ by the expression

$$\Xi^s = \exp\left(\frac{-A\zeta}{kT}\right) = \exp\left(\frac{-N^s\zeta\alpha}{kT}\right), \tag{21}$$

where A is the surface area and α is the mean area of the surface per atom and is defined as $\alpha = A/N^s$, and N^s is the total number of atoms at the surface; k is the Boltzmann constant.

Prasad *et al.* [21] gave the expression for surface tension of the binary alloys in terms of activity co-efficient of the alloy components as

$$\zeta = \zeta_A + \frac{kT}{\alpha}\ln\frac{c_A^s}{c_A} - \frac{kT}{\alpha}\ln\gamma_A + [p(c_B^s)^2 + q(c_B)^2]\frac{w}{\alpha}, \tag{22}$$

$$\zeta = \zeta_B + \frac{kT}{\alpha}\ln\frac{c_B^s}{c_B} - \frac{kT}{\alpha}\ln\gamma_B + [p(c_A^s)^2 + q(c_A)^2]\frac{w}{\alpha}, \tag{23}$$

where ζ_A and ζ_B are surface tension values for the pure components A and B respectively. c_i and c_i^s are the bulk and surface concentrations of the alloy components respectively. γ_A and γ_B are the bulk activity co-efficients of the alloy components. w is the interchange energy.

The surface $S_{\mathrm{cc}}(0)$ can be written as [22]

$$S_{\mathrm{cc}}^s(0) = c_A^s c_B^s\left[1 + \left(\frac{z^s}{2\beta^s}\right)(1-\beta^s)\right]^{-1}, \tag{24}$$

where

$$\beta^s = \left\{1 + 4c_A^s c_B^s\left[\exp\left(\frac{2w}{z^s kT}\right) - 1\right]\right\}^{1/2}. \tag{25}$$

Here, z^s is the coordination number of the surface atoms which is obtained from $z^s = (p+q)z$ and z is the coordination number in the bulk.

3. Results and discussions

The model of Singh and Sommer [17] was used to investigate the concentration dependence of some thermodynamic quantities of Ag–Sb and Ag–In liquid alloys. By varying the parameter n and W/RT, a simultaneous overall fit of the experimental activity and Gibb's free energy of mixing (G_m) was obtained for the two alloys, respectively. The values of n and W/RT used to obtain these fits for the two alloys are given in Table 1. These values of parameters were now used in subsequent expressions to obtain other thermodynamic quantities such as activity coefficients, concentration–concentration fluctuation at the long wavelength limit ($S_{\mathrm{cc}}(0)$) and the Warren–Cowley short-range order parameter (α_1) for the alloys.

In Figure 1, the calculated activity and free energy values for Ag–Sb are compared with experimentally determined values taken from [16]. In Figure 2, the calculated activity and

Table 1. Model parameters for Ag–Sb and Ag–In liquid alloys.

Alloy	T (K)	n	$\frac{W}{RT}$
Ag–Sb	1073	0.145	−3.09
Ag–In	1200	0.240	−0.09

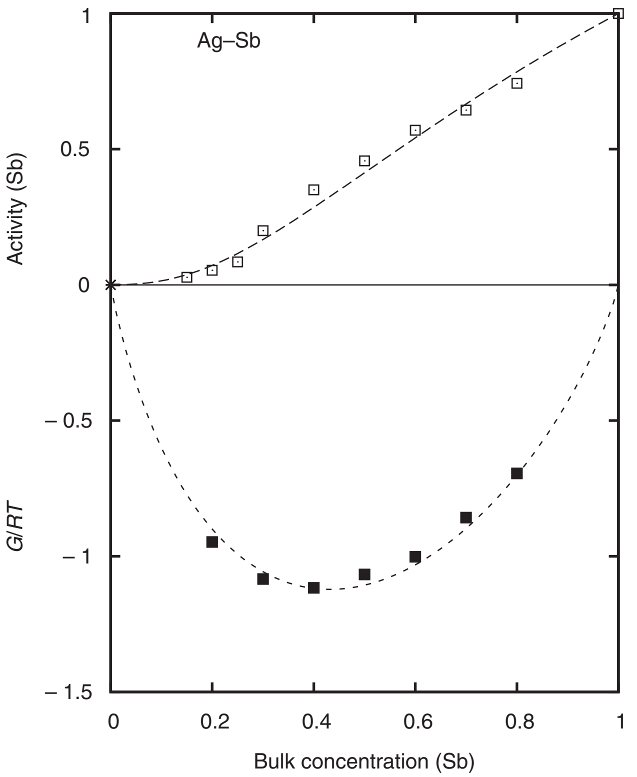

Figure 1. Activity of Sb and integral Gibbs free energy of mixing (G/RT) *vs*. bulk concentration of Sb for Ag–Sb liquid alloy. Lines represent calculated values while points are experimental values at 1073 K from [16].

free energy values for Ag–In are also compared with experimentally determined values taken from [1]. The behaviour of the activity values for both alloys appear similar, approaching ideal values above 0.3 atomic fraction of Sb and In for both alloys, respectively. The slight negative departure from ideality at low concentrations of Sb and In for the respective alloys suggests some low level of order in the alloy, especially at that region. However, in the phase diagrams of Ag–Sb and Ag–In [23], no intermetallic compounds were suggested; hence our calculations were carried out using the statistical model based on formation of clusters of self associates. The calculated values of activity and free energy of mixing using this model had an excellents fit with experiments for both alloys. The plots show that both alloys have similar behaviour, exhibiting some slight asymmetry about equiatomic concentration for the free energy of mixing plots.

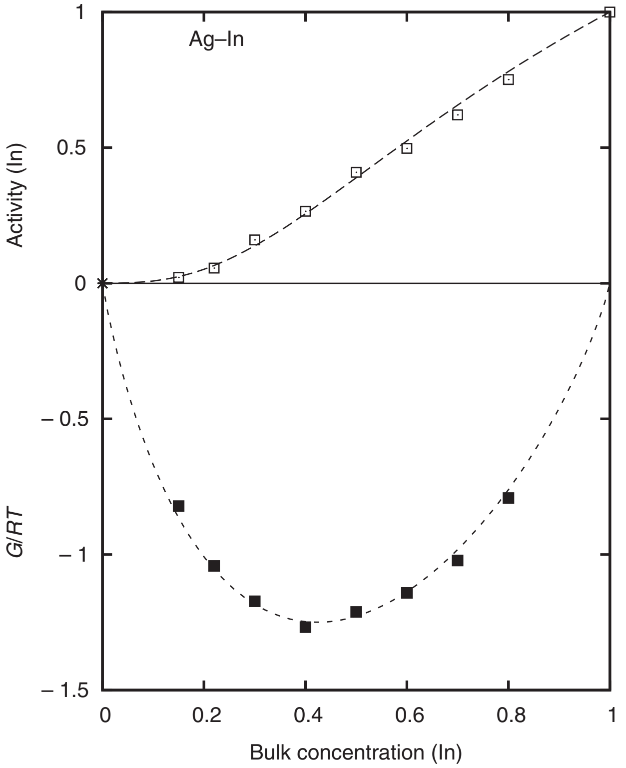

Figure 2. Activity of In and integral Gibbs free energy of mixing (G/RT) *vs.* bulk concentration of In for Ag–In liquid alloy. Lines represent calculated values while points are experimental values at 1200 K from [1].

To understand better the interactions in the systems with respect to the nature of ordering among the atomic species, the concentration–concentration fluctuation at the long wavelength limit ($S_{cc}(0)$) was obtained using the thermodynamic parameters already determined. The values of $S_{cc}(0)$ obtained from experimental values were used to compare with the calculated values. $S_{cc}(0)$ can be obtained from the experimental free energy values or expressed in terms of the activities of the alloy components a_A and a_B as

$$S_{cc}(0) = RT\left(\frac{\partial^2 G_m}{\partial c_A^2}\right)^{-1}_{T,P,N} = c_B a_A\left(\frac{\partial a_A}{\partial c_A}\right)^{-1}_{T,P,N} = c_A a_B\left(\frac{\partial a_B}{\partial c_B}\right)^{-1}_{T,P,N}. \qquad (26)$$

Here the experimental activity data for both alloys was fitted to higher order polynomials and their derivatives were obtained and used in the above expression to obtain the required experimental $S_{cc}(0)$ values.

Figure 3 shows the $S_{cc}(0)$ and Warren–Cowley short-range order parameter (α_1). In the figure, the calculated $S_{cc}(0)$ for Ag–Sb and Ag–In alloys are presented. The open blocks are experimental values for Ag–Sb while the solid blocks are experimental values for Ag–In. The dots are ideal values. The solid line represents the calculated values for Ag–Sb while the broken lines are for Ag–In. It is clear from the figure that the $S_{cc}(0)$ values are below ideal values throughout the concentration range for both alloys suggesting some

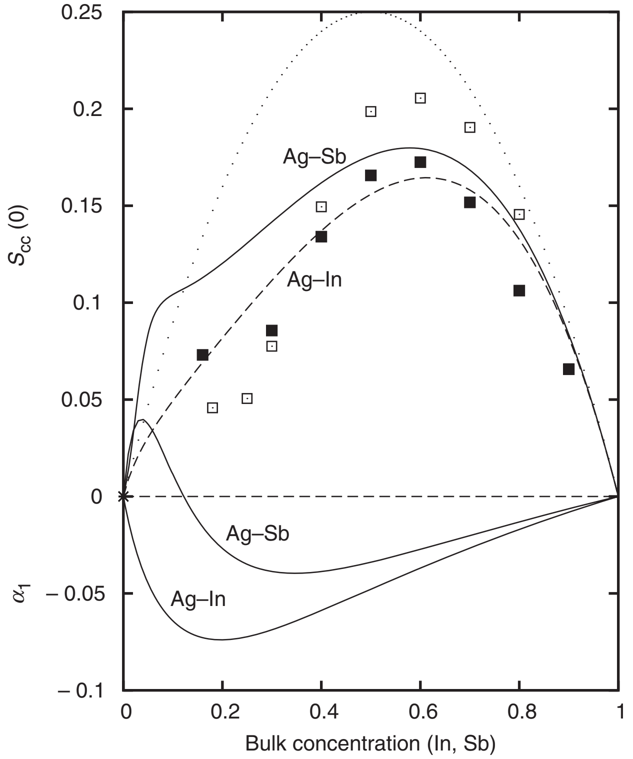

Figure 3. Bulk $S_{cc}(0)$ and Warren–Cowley short-range order parameter (α_1) *vs.* bulk concentration of In/Sb for Ag–In and Ag–Sb liquid alloys, respectively. Lines represent calculated values. Open blocks are experimental values for Ag–Sb while solid blocks are experimental values for Ag–In.

form of order existing in these alloys of silver. The level of ordering is higher below equiatomic composition for both alloys while above, the alloys tend towards ideal mixing as depicted by the α_1 plot. However, below 0.1 atomic fraction of Sb, the calculated $S_{cc}(0)$ for Ag–Sb showed somewhat higher values than ideal values; hence suggesting some small tendency to phase separation in that region. The calculated values of $S_{cc}(0)$ for both alloys show a qualitative trend, with values derived from experimental data and the α_1 values indicating that the ordering tendency is weak. Further, maximum order in these alloys will occur at about 0.35 atomic fraction of Sb for Ag–Sb with $\alpha_1^{\min} \approx -0.039$, while that for Ag–In occurs at about 0.2 atomic fraction of In with $\alpha_1^{\min} \approx -0.073$. Obviously from the figure, the ordering in Ag–In is stronger than in Ag–Sb. Ag–In must have stronger tendencies to compound formation than Ag–Sb.

To calculate the mutual diffusion coefficient D_m for the Ag–Sb and Ag–In liquid alloys, the expression in Equation (11) was used. The values of the self diffusion coefficients of the pure alloy components Ag, Sb, and In, at the temperatures of 1073 and 1200 K for Ag–Sb and Ag–In respectively, are required. Since the experimental values of diffusion co-efficent of these components at temperatures of interest are not available, the model of Protopapas *et al.* [4] given in Equation (13) was used to estimate values of diffusion co-efficent for these alloy components. Iida and Guthrie [3] compared values obtained using this model with experimental values for some liquid metals at their melting point. The calculated

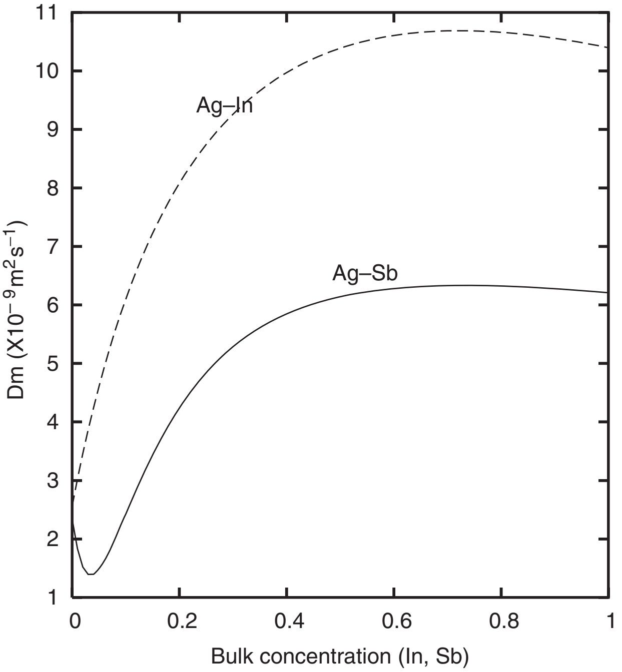

Figure 4. Mutual diffusivities, D_m ($\times 10^{-9}$m^{2}s^{-1}) *vs.* bulk concentration of In/Sb for Ag–In and Ag–Sb liquid alloys, respectively.

results were comparable with experimental values. The values of M, ρ_m and Λ in the model of Protopapas *et al.* were obtained from [4]. Figure 4 shows the variation of mutual diffusion co-efficent with bulk concentration of Sb and In for Ag–Sb and Ag–In liquid alloys at 1073 and 1200 K, respectively. The plots show that the mutual diffusivities for both alloys showed pronounced increases in value with increasing Sb and In concentrations, respectively, until above equiatomic concentration, where further increases in the concentrations of Sb and In in the respective alloys resulted in very small or insignificant changes in diffusivities. The diffusivities of Ag–In which showed higher tendencies to heterocoordination manifested higher values over the whole concentration range than values for Ag–Sb. For the Ag–Sb liquid alloy, the calculated $S_{cc}(0)$ and the short-range order parameter (α_1) showed indication of some small form of homocoordination below 0.1 atomic fraction Sb, the mutual diffusivity of this alloy showed small decrease in values within this region. It is therefore possible to infer from our calculations that tendencies toward heterocoordination result in an increase in mutual diffusivities while tendencies toward homocoordination lead to a decrease in mutual diffusivities.

The viscosities of Ag–Sb and Ag–In were calculated over the whole concentration range using the expression of Kucharsky [20] given in Equation (17). The values of viscosities and atomic volumes for the alloy components were obtained from [3]. The activity co-efficent was obtained from our calculations using Equation (5) and the energy parameters given in Table 1. In Figure 5, the calculated viscosity values for Ag–Sb and Ag–In alloys at 1073 and 1200 K are presented. The solid line represents calculated values of viscosity for an Ag–Sb liquid alloy while the points are experimental values of viscosity for Ag–Sb at 1273 K obtained from [3]. The solid line calculated for the value of $m = 4.5$ showed some reasonable agreement with experiment above 0.5 atomic fraction of Sb. Below this concentration, there is only a qualitative trend between experiment and calculations. However, we note that the experimental values were obtained at 1273 K while the calculated values were for 1073K. At a lower temperature of 1073 K, the measured values of viscosity is expected to be higher and may approach the calculated values. All broken lines in the figure are the calculated values of viscosity for Ag–In liquid alloys for values of fitting parameter $m = 3.5$, 1.5, 0.1 and −0.5. There are no experimental values for Ag–In available for comparison with calculated values. From our earlier calculations of activities, free energy of mixing, $S_{cc}(0)$ and diffusivities for Ag–Sb and Ag–In alloys, it can be said that these alloys manifest close behaviours in their thermophysical properties which follow the same trend. If we assume that this observation holds true for the viscosity of these alloys, then the viscosity values of Ag–In across the concentration range will follow the trend of the values for Ag–Sb. Hence, the viscosity values for Ag–In can be estimated for m values within the range $1.5 \leq m \leq 4.0$. Within this range of m, the viscosity isotherms for Ag–In follow the trend of the calculated viscosity values for Ag–Sb, hence it is expected that the 'real' viscosity values of Ag–In may be described within these values of the fitting parameter m. Figure 5 also shows a minimum in the viscosity isotherms of Ag–Sb and Ag–In at about 0.7 atomic fraction of In, Sb. From the $S_{cc}(0)$ curves for these alloys in Figure 3, the alloys appear to be close to ideal mixing at above 0.7 atomic fraction of In,Sb and are heterocoordinated below this concentration. The minimum viscosity

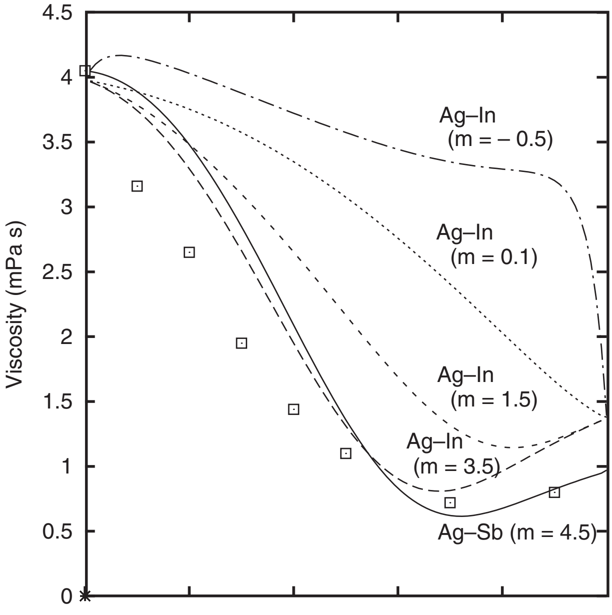

Figure 5. Viscosity *vs.* bulk concentration of In/Sb for Ag–In and Ag–Sb liquid alloys. Solid line is the calculated values for Ag–Sb at $m = 4.5$. Broken lines are calculated values for Ag–In at $m = 3.5, 1.5, 0.1$ and -0.5. Points are experimental values for Ag–Sb at 1273 K from [3].

observed about this concentration may be due to structural readjustment of alloy components as the alloys transited from ideal mixture to a former compound.

The surface compositions and surface tension values of Ag–Sb and Ag–In liquid alloys were numerically computed from Equations (22) and (23). The activity co-efficients for the Ag, Sb and In atoms in Ag–Sb and Ag–In liquid alloys, respectively, at the temperatures of investigation were computed from the expression in Equation (5). The surface coordination fractions p and q are taken as those for closed packed structures with $p = 0.5$ and $q = 0.25$ for all systems considered. The surface tension (ζ_i) and atomic volume (Ω_i) at the melting temperature of the components of the alloy systems were taken from [3], (where i denotes the components Ag, Sb or In of the alloys). However, to obtain the surface tension and atomic volume at the working temperature of 1073 K, and 1200 K for the Ag–Sb and Ag–In alloys, respectively, the relationship on the temperature dependence of surface tension and atomic volume as given in [24] was used and is given as,

$$\zeta_i = \zeta_{im} + (T - T_m)\frac{\partial \zeta_i}{\partial T}, \tag{27}$$

and

$$\Omega_i = \Omega_{im}[1 + \theta(T - T_m)], \tag{28}$$

where θ is the thermal co-efficient of expansion, Ω_{im} and ζ_{im} are the atomic volumes and surface tension of the alloy components at their melting temperature T_m and T is the working temperature in Kelvins. The values of $\partial\zeta_i/\partial T$ and θ for the pure components of the alloy are obtained from [3]. The atomic surface area α_i for each atomic species of the different alloy systems was calculated following the relation [25]

$$\alpha_i = 1.102\left(\frac{\Omega_i}{N}\right)^{2/3}, \tag{29}$$

and the mean surface area α is then given as

$$\alpha = \sum_i c_i \alpha_i, \tag{30}$$

where N is Avogadro's number and c_i are the concentrations of the alloy components.

Figure 6 shows the plots of surface concentration of Sb and In against their respective bulk concentration for Ag–Sb and Ag–In liquid alloys, respectively. For the Ag–Sb liquid alloys, the Sb atoms segregate to the surface at above 0.4 atomic fraction of Sb. But in Ag–In, complete segregation of In atoms to the surface was not predicted by our calculations, however, more In atoms are expected at the surface than Ag atoms. The surface tension values for both alloys (Figure 7) shows a similar trend, decreasing with increasing bulk concentration of Sb and In respectively. There are no available experimental surface tension values for these alloys to compare with experiment, however, it has been shown that calculations with this model produce values comparable with experiment [26,27]. The calculated surface tension values for Ag–Sb are higher than the values for Ag–In at higher concentrations of Ag while at lower concentrations of Ag, the surface tension values for Ag–Sb become lower than the values for Ag–In. The surface $S_{cc}(0)$ of Ag–In (Figure 8) shows indications of some level of heterocoordination at the surface as its

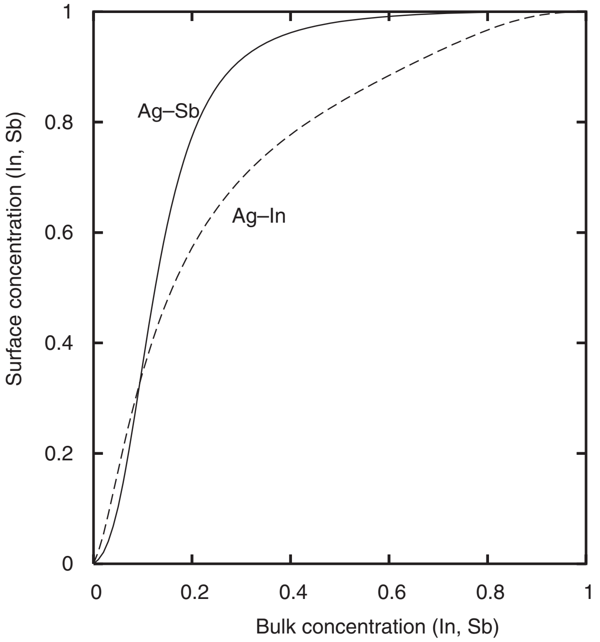

Figure 6. Surface concentration of In/Sb *vs.* bulk concentration of In/Sb for Ag–In and Ag–Sb liquid alloys, respectively. Solid line is values for Ag–Sb and broken lines are values for Ag–In.

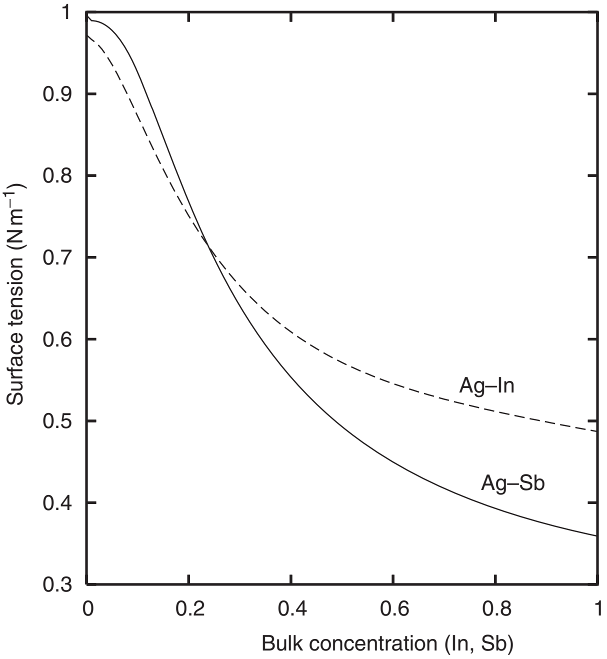

Figure 7. Surface tension *vs.* bulk concentration of In/Sb for Ag–In and Ag–Sb liquid alloys, respectively. Solid lines is values for Ag–Sb while broken line are values for Ag–In.

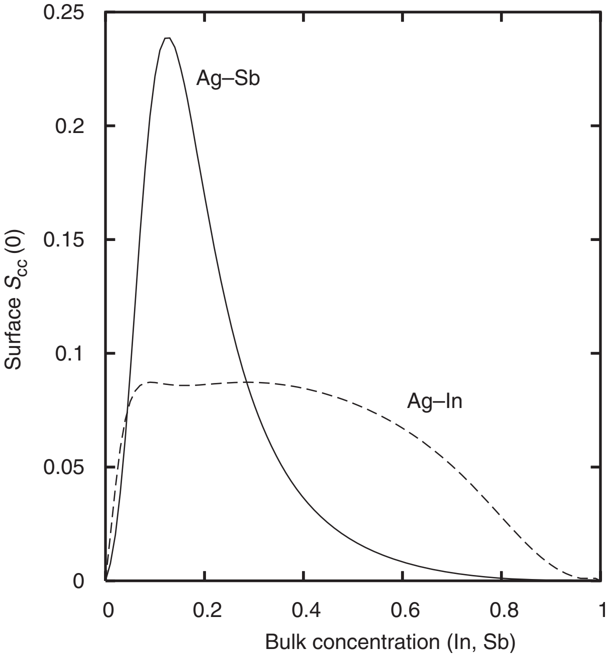

Figure 8. Surface $S_{cc}(0)$ *vs.* bulk concentration of In/Sb for Ag–In and Ag–Sb liquid Alloys, respectively. Solid line is values for Ag–Sb while broken lines are values for Ag–In.

broadened peak is very much less than the ideal value peak of 0.25. The surface $S_{cc}(0)$ values for Ag–Sb are closer to ideal values indicating a tendency to regular mixture of alloy components at the surface.

4. Conclusion

The thermophysical properties of the liquid alloys Ag–Sb and Ag–In appear to exhibit similar behaviours. Ag–In has a greater tendency to compound formation than Ag–Sb. The compound forming tendencies of Ag–In appear to be stronger at the surface than in the bulk. On the other hand, Ag–Sb exhibited some low level of ordering in the bulk but has a strong tendency toward regular mixture of alloy components at the surface

Acknowledgement

B.C. Anusionwu acknowledges the Director of the Abdus Salam International Centre for Theoretical Physics for financial support as associate member of the Centre.

References

[1] D. Jendrzejezyk and K. Fitzner, Thermochim. Acta **433**, 66 (2005).
[2] R. Novakovic, T. Tanaka, M.L. Muolo, J. Lee, and A. Passerone, Surf. Sci. **591**, 56 (2005).
[3] T. Iida and R.I.L. Guthrie, *The Physical Properties of Liquid Metals* (Clarendon Press, Oxford, 1988).

[4] P. Protopapas, H.C. Anderson, and N.A.D. Parlee, J. Chem. Phys. **59**, 15 (1973).
[5] T. Tanaka, N.A. Gocken, and Z. Morita, Z. Metallkd. **81**, 49 (1999).
[6] F. Sommer, R.N. Singh, and V. Witusiewicz, J. Alloys Compd. **325**, 118 (2001).
[7] T. Tanaka, N.A. Gocken, Z. Morita, and T. Iida, Z. Metallkd. **84**, 192 (1993).
[8] N. Eustathopoulos, M. Nicholas, and B. Drevet, *Wettability at High Temperatures,* 3 vols. (Pergamon Materials Series, Oxford, UK, Pergamon, 1999).
[9] W. Gluchowski and Z.M. Rdzawski, J. Achiev. Mater. Manuf. Engr. **28**, 143 (2008).
[10] T. Nozaki, M. Shimoji, and K. Niwa, Trans. JIM **7**, 52 (1966).
[11] K. Kameda, Y. Yoshida, and S. Sakairi, J. Jpn. Inst. Met. **45**, 614 (1981).
[12] C. Castanet, Y. Claire, M. Gilbert, and G. Laffitte, Rev. Hautes Temper. Refract. **7**, 51 (1970).
[13] B. Predel and A. Emam, Z. Metallkd. **64**, 496 (1973).
[14] M. Hino, T. Azakami, and M. Kameda, J. Jpn. Inst. Met. **39**, 1175 (1975).
[15] T. Nozaki, M. Shimoji, and K. Niwa, Ber Bunsenges **70**, 207 (1966).
[16] A. Krzyzak and K. Fitzner, Thermochim. Acta **414**, 115 (2004).
[17] R.N. Singh and F. Sommer, Z. Metallkd. **83**, 553 (1992).
[18] L.S. Darken, Trans. AIME **175**, 184 (1948).
[19] L.C. Prasad, R.N. Singh, V.N. Singh, and G.P. Singh, J. Phys. Chem. B **102**, 921 (1998).
[20] M. Kucharsky, Z. Metallkd. **77**, 393 (1986).
[21] L.C. Prasad, R.N. Singh, and G.P. Singh, Phys. Chem. Liq. **27**, 179 (1994).
[22] L.C. Prasad and R.N. Singh, Phys. Rev. B **44**, 13768 (1991).
[23] W.G. Moffatt, *The Handbook of Binary Phase Diagrams* (General Electric Company, Schenectady, NY, 1980).
[24] C.J. Smithells and E.A. Brandes, editors, *Metals Reference Book*, 5th ed. (Butterworths, London, 1978).
[25] P. Laty, J.C. Joud, and P. Desre, Surf. Sci. **60**, 109 (1976).
[26] B.C. Anusionwu, O. Akinlade, and L.A. Hussain, J. Alloys Compds. **278**, 175 (1998).
[27] R. Novakovic, E. Ricci, D. Guiranno, and A. Passerone, Surf. Sci. **576**, 175 (2005).