

Theoretical studies of mutual diffusivities and surface properties in Cd–Ga liquid alloys

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Abstract. The mutual diffusion coefficients, activation energy for diffusion, surface concentration and surface tension of the liquid Cd–Ga alloys have been calculated throughout the concentration range using energetics obtained from the theoretical model fits of the experimental thermodynamic data. Our calculations show that Cd–Ga liquid alloys showed immiscibility at a temperature of 723 K between 0.4 and 0.5 atomic fraction of Cd. Within this concentration region and temperature, the mutual diffusion coefficients approached zero values and the activation energy for diffusion reached high peak values of 220 J/mol. It was also observed that within the region of immiscibility, the diffusion coefficients do not obey Arrhenius relation over a wide range of temperature.

Keywords. Mutual diffusivities; surface properties; Cd–Ga liquid alloys.

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1. Introduction

Investigations of surface and transport properties of liquid binary alloys have been a subject of research [1–6]. The knowledge of the atomic transport and surface properties of liquid alloys are important as they are used in many fields of engineering and in metallurgical processes. For instance, surface tension is a dominating factor for phenomena such as gas absorption, nucleation of gas bubbles, nucleation and growth of nonmetallic inclusions and slag/metal reactions [7]. On the other hand, the distribution of solute in a solid or liquid solution is dependent on mass transport which is controlled by atomic diffusion phenomena.

Incidentally, the experimental data on some transport and surface properties of liquid alloys such as diffusivities, surface tension and surface concentrations are scanty due to problems associated with experimental work [7]. An alternative then is to estimate these important sets of data using theoretical models. In line with these needs, many authors have developed different models to determine transport and surface properties such as diffusivities, viscosities, surface tension and surface concentrations [8–13] from hard sphere, statistical or phenomenological point of

view. Some of these models require inputs from thermodynamic measurements such as order energy, activity or activity coefficients for the determination of these properties, thus underlining the importance of thermodynamic studies for liquid binary alloys.

In this study, the transport and surface properties of Cd–Ga liquid alloys are determined from energetics and derivatives from experimental thermodynamic data. Cd–Ga alloys have been studied by many authors [14–16]. The alloy is monotectic and showed immiscibility gap in the liquid state according to the phase diagrams [17,18]. The experimental study by Shamsuddin *et al* [15] showed that the values of Darken’s stability is slightly positive within the concentration range $0.25 < x_{\text{Cd}} < 0.45$ indicating poor stability and in other words predicting immiscibility within this region. This experimental thermodynamic data of Shamsuddin *et al* [15] which covered the range of temperatures from 723 to 851 K provides information to study how temperature affects mutual diffusivities, surface properties and immiscibility in this alloy.

2. Theoretical models

2.1 Thermodynamic properties

Singh and Sommer [19] proposed a simple statistical model for studying phase separating binary liquid alloys. This model assumes that a liquid binary A–B alloy consisting of N_A atoms of element A and N_B atoms of element 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 depend on the number of self-associates ($n = \mu/\nu, \mu > \nu$). Using the quasi-chemical approximation, an expression for the Gibbs free energy is obtained as

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

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

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

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

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

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

where R is the molar gas constant and the activity coefficients (γ_i) can be obtained from the relation $\gamma_i = a_i/c_i$.

To obtain the heat of mixing and entropy of mixing for the alloy using this model, the standard thermodynamic relation given below is employed:

$$H_m = G_m + TS_m, \quad (5)$$

where $S_m = -(\partial G_m/\partial T)_P$ is the entropy of mixing. From eq. (1) we obtain the derivative of the free energy of mixing G_m as

$$\frac{\partial G_m}{\partial T} = R[c \ln c + (1 - c) \ln(1 - c) + c \ln(1 - \xi) + \ln \Gamma] + c(1 - c)\Gamma \frac{\partial W}{\partial T}. \quad (6)$$

Here, the energy parameter W was taken as temperature-dependent. The entropy of mixing can now be obtained from eq. (5) as $S_m = (H_m - G_m)/T$.

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

$$S_{cc}(0) = RT \left(\frac{\partial^2 G_m}{\partial c^2} \right)_{T,P,N}^{-1}. \quad (7)$$

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

$$S_{cc}(0) = \frac{c(1 - c)}{1 - c(1 - c)g(n, W)}, \quad (8)$$

where

$$g(n, W) = \frac{2n^2(W/RT) - (n - 1)^2[c + n(1 - c)]}{[c + n(1 - c)]^3}. \quad (9)$$

2.2 Transport properties

Using Darken's thermodynamic equation for diffusion [20], 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 [19,21]

$$\frac{D_M}{D_{id}} = \frac{S_{cc}^{id}(0)}{S_{cc}(0)}, \quad (10)$$

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

$$D_{id} = cD_B + (1 - c)D_A, \quad (11)$$

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 eq. (10) if the self-diffusivities D_i are known from experiment. Since knowledge of 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* [12] for the determination of self-diffusivities of liquid metals based on the hard sphere model. The expression for diffusivities is given as

$$D = \sigma C_{AW}(\eta) \left(\frac{\pi RT}{M} \right)^{1/2} \frac{(1 - \eta)^3}{8\eta(2 - \eta)}, \quad (12)$$

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 expression:

$$\sigma = 1.126\sigma_m \left[1 - 0.112(T/T_m)^{1/2} \right], \quad (13)$$

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

$$\sigma_m = 1.41(M/\pi\rho_m N_A)^{1/2}, \quad (14)$$

where 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

$$\eta = \frac{0.472\rho\sigma^3}{\rho_m\sigma_m^3}, \quad (15)$$

where 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 [7,12].

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* [22] to obtain expressions for surface properties. The surface grand partition function Ξ^s is related to the surface tension ξ by the expression

$$\Xi^s = \exp\left(\frac{-A\xi}{kT}\right) = \exp\left(\frac{-N^s\xi\alpha}{kT}\right), \quad (16)$$

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* [22] gave the expression for surface tension of the binary alloys in terms of activity coefficient of the alloy components as

$$\xi = \xi_A + \frac{kT}{\alpha} \ln \frac{c_A^s}{c_A} - \frac{kT}{\alpha} \ln \gamma_A + [p(c_B^s)^2 + q(c_B)^2] \frac{w}{\alpha} \quad (17)$$

$$\xi = \xi_B + \frac{kT}{\alpha} \ln \frac{c_B^s}{c_B} - \frac{kT}{\alpha} \ln \gamma_B + [p(c_A^s)^2 + q(c_A)^2] \frac{w}{\alpha}, \quad (18)$$

where ξ_A and ξ_B are the 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 coefficients of the alloy components and w is the interchange energy.

The surface $S_{cc}(0)$ can be written as [23]

$$S_{cc}^s(0) = c_A^s c_B^s \left[1 + \left(\frac{z^s}{2\beta^s} \right) (1 - \beta^s) \right]^{-1}, \quad (19)$$

where

$$\beta^s = \left\{ 1 + 4c_A^s c_B^s \left[\exp \left(\frac{2w}{z^s kT} \right) - 1 \right] \right\}^{1/2}. \quad (20)$$

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

3.1 Thermodynamic properties

The concentration dependence of some thermodynamic quantities of the Cd–Ga liquid alloys were investigated using the model of Singh and Sommer [19]. In this model, the values of the parameters n (ratio of self-associates) and W/RT (order energy) were obtained by a simultaneous overall fit of the experimental activity and Gibb's free energy of mixing (G_m) at different temperatures of investigation. To obtain the values of heat of mixing (H_m) and entropy (S_m), an extra parameter $1/R(\partial W/\partial T)$ being the derivative of the order energy is required. The values of n , W/RT and $1/R(\partial W/\partial T)$ obtained at different temperatures are given in table 1.

Table 1. Model parameters for Cd–Ga liquid alloy.

T (K)	n	W/RT	$(1/R)(\partial W/\partial T)$
723	0.89	2.11	–
801	0.89	1.97	–
851	0.91	1.87	0.58

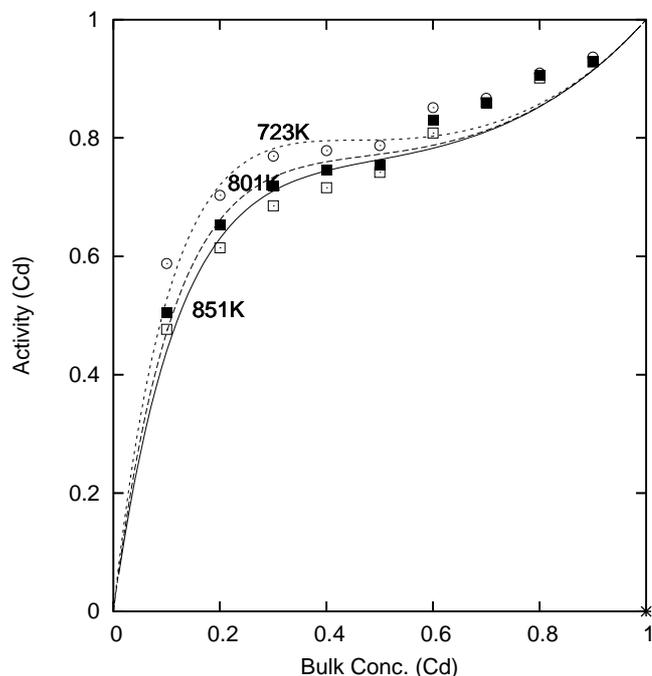


Figure 1. Activity of Cd vs. atomic fraction of Cd for Cd–Ga liquid alloy. Open blocks are experimental values at 851 K, solid blocks are experimental values at 801 K, while open circles are experimental values at 723 K. Solid lines are the calculated values at 851 K, long broken lines are the calculated values at 801 K and short broken lines are calculated values at 723 K.

Using these energy parameters, other thermodynamic quantities such as the concentration fluctuation at the long wavelength limit $S_{cc}(0)$ and activity coefficients are determined and will be used in subsequent calculations of some transport and surface properties of the alloy.

The experimental data used in the calculation of the thermodynamic properties of Cd–Ga liquid alloy at 723, 801 and 851 K were from the work of Shamsuddin *et al* [15]. In figures 1 and 2, the calculated activity and free energy values were compared with experimental values. It can be observed that there are some reasonable agreement between the calculated and experimental values especially below 0.6 atomic fraction of Cd. Above this concentration, the calculated values have some form of qualitative trend with experimental values. In general, the overall fit of the data is reasonable. On the other hand, the calculated heat of mixing and entropy values for Cd–Ga alloys had an excellent agreement with experiment at 851 K (experimental values at other temperatures were not available). This is shown in figure 3. Both the heat of mixing and entropy values are symmetric about equiatomic concentration unlike the Gibb’s free energy where the calculated values showed some form of asymmetry. Table 1 shows an increase in the ratio of the number of associates n at temperature 851 K, suggesting that at higher temperatures,

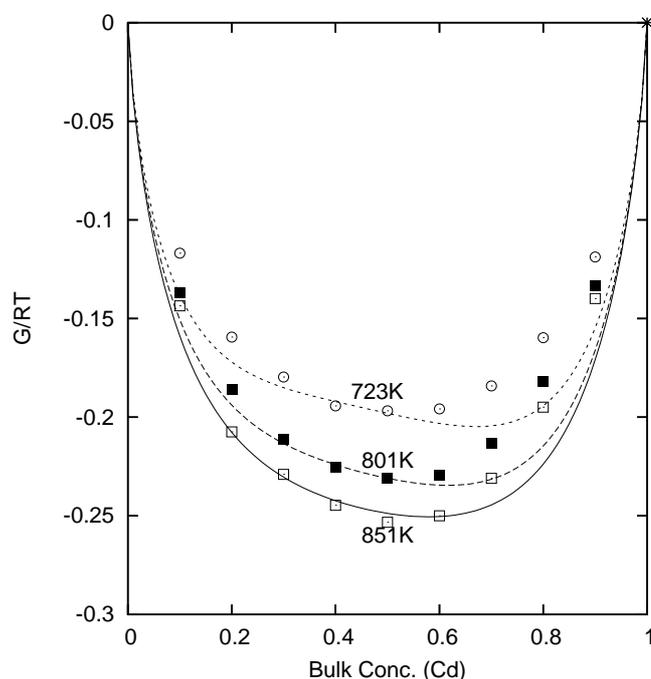


Figure 2. $\Delta G/RT$ vs. atomic fraction of Cd for Cd–Ga liquid alloy. Open blocks are experimental values at 851 K, solid blocks are experimental values at 801 K, while open circles are experimental values at 723 K. Solid lines are the calculated values at 723 K, long broken lines are the calculated values at 801 K and short broken lines are calculated values at 851 K.

it is likely that the number of self-associates in Ga clusters may be decreasing at a faster rate than that in Cd. Ga has a lower melting point of 302 K while Cd has a melting point of 594 K. Hence at 851 K, Ga had experienced a larger temperature deviation from melting point than Cd. This higher temperature difference may be responsible for the suspected faster dissociation rate of Ga clusters at high temperatures. The pronounced positive departure of activity values from ideality at a higher temperature of 851 K indicates that the local order in Cd–Ga liquid alloy is very strong.

The strength of segregation is determined by the extent of positive departure of the concentration fluctuation at the long wavelength limit $S_{cc}(0)$ from its ideal values $S_{cc}^{id}(0) = c(1 - c)$. c is the concentration of the A atom in the A–B liquid alloy. To determine the strengths of segregation in the Cd–Ga alloy at different temperatures, the concentration fluctuation at the long wavelength limit $S_{cc}(0)$ calculated from eq. (8) is used. The experimental values of $S_{cc}(0)$ was also determined. These values were compared with the calculated values of $S_{cc}(0)$. The values of experimental $S_{cc}(0)$ are obtained from measured activity values [15] through the usual relation,

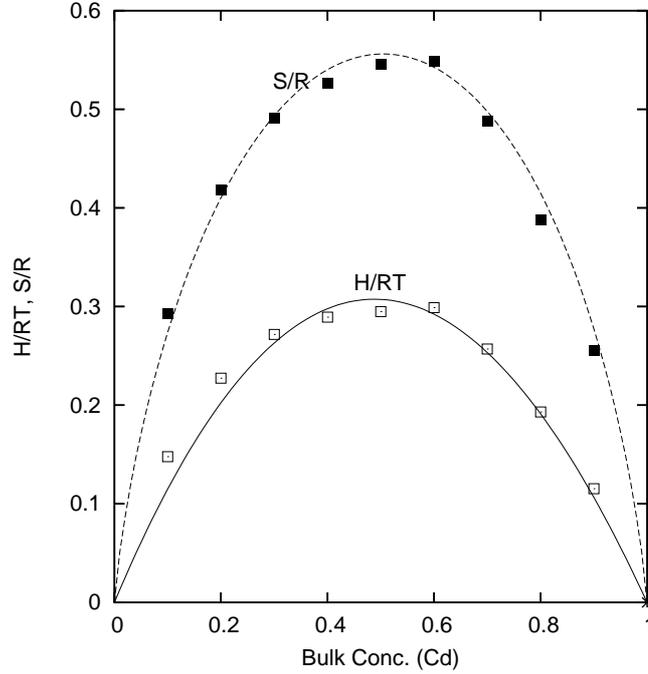


Figure 3. Heat of mixing ($\Delta H/RT$) and entropy ($\Delta S/R$) vs. bulk atomic fraction of Cd for Cd–Ga liquid alloy. Points represent experimental values. Lines are the corresponding calculated values.

$$S_{cc}(0) = \frac{(1 - c)a_{Cd}}{(\partial a_{Cd}/\partial c)_{T,P}}. \quad (21)$$

Here, the experimental activity data were fitted to higher-order polynomials. Their derivatives were obtained and used in the above expression to obtain the required experimental values of $S_{cc}(0)$.

Figure 4 shows comparison of the calculated $S_{cc}(0)$ with the experimental values for the three temperatures under investigation. There are some qualitative agreement between experimental values and calculated values at the three temperatures of interest. At temperature 723 K, the $S_{cc}(0)$ values approached very large values within the concentration region $0.35 < c_{Cd} < 0.65$. This is an indication that within this concentration range and at temperature 723 K, Cd–Ga showed tendency to immiscibility. Shamsuddin *et al* [15] had earlier pointed out that immiscibility in Cd–Ga could occur between the concentration $0.25 \leq c_{Cd} \leq 0.45$. Our calculations show that the immiscibility will be reduced rapidly with increase in temperature as the temperature is increased from 723 to 851 K. The observed trend in the reduction of the peak value of $S_{cc}(0)$ suggests some form of exponential reduction in the strength of segregation in this alloy as the temperature increases. This trend further suggests that with further increase in temperature, the $S_{cc}(0)$ values of the alloy may approach ideal values. The reduction in the strength of the segregation and immiscibility could be associated with the dissociation of segregating clusters

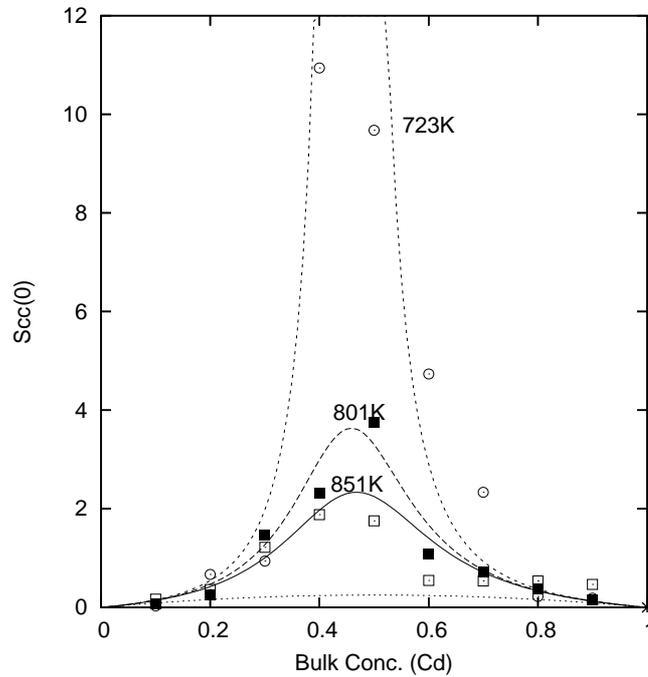


Figure 4. Bulk $S_{cc}(0)$ vs. atomic fraction of Cd for Cd–Ga liquid alloy. Open blocks are experimental values at 851 K, solid blocks are experimental values at 801 K, while open circles are experimental values at 723 K. Solid lines are the calculated values at 851 K, long broken lines are the calculated values at 801 K and short broken lines are the calculated values at 723 K. Dots are ideal values.

of the liquid alloy components. This dissociation occurs as a result of thermal agitation associated with increase in the temperature of the liquid alloy. The parameter n in table 1 suggests that the Ga cluster dissociates at a faster rate as the temperature of the alloy increases. The immiscibility behaviour and different rates of dissociation of clusters of self-associates make Cd–Ga far from being a simple segregating liquid binary alloy.

3.2 Transport properties

The mutual diffusion coefficient D_m for the Cd–Ga liquid alloy was calculated at temperatures 723, 801 and 851 K using eq. (10). Here, the values of self-diffusion coefficients of pure alloy components Cd and Ga at the mentioned temperatures are required. Since the experimental values of diffusion coefficient for Cd and Ga at these temperatures are not available, the model of Protopapas *et al* [12] given in eq. (12) was used to estimate the values of diffusion coefficient for these alloy components. We show in table 2, the comparison of experimental diffusion coefficient at melting point with our own values calculated at the melting point

Table 2. Comparison of experimental self-diffusivities of liquid metals at melting point with calculated values from the model of Protopapas [12].

Metals	Experimental ($10^{-9} \text{ m}^2 \text{ s}^{-1}$)	Calculated ($10^{-9} \text{ m}^2 \text{ s}^{-1}$)
Cd	1.78	1.956
Ga	1.71	1.745
In	1.68	1.756
Li	6.80	6.946
Na	4.23	4.245
Pb	1.68	1.648
Sn	2.05	1.947

using the model of Protopapas *et al* [12]. The experimental values of diffusion coefficients at the melting point of metals were obtained from the compilation of Iida and Guthrie [7]. Our calculated values are reasonably close to experimental values. Hence we use the model to predict the values of diffusion coefficient for the alloy components at 723, 801 and 851 K. The values of M , ρ_m and Λ are obtained from ref. [7]. Figure 5 shows the variation of mutual diffusion coefficient with bulk concentration of Cd for the Cd–Ga alloy at 723, 801 and 851 K. All plots show a pronounced decrease of diffusion coefficient with increase in Cd concentrations until a minimum value is reached between 0.4 and 0.5 atomic fraction of Cd. At 723 K, the diffusion coefficient approached zero within this range of concentrations. Our results suggest that diffusion-related activities within this region at all the temperatures will be very low. Note that this is the region where the peaks of the $S_{cc}(0)$ values exist. It is also the region where immiscibility is expected in the alloy at 723 K. We also infer from our results that phase segregation in a liquid binary alloy leads to reduction in mutual diffusion coefficients and will negatively affect diffusion-related activities in the alloy.

Diffusion coefficient varies with temperature according to Arrhenius law given as

$$D = D_0 \exp\left(\frac{-Q_D}{RT}\right), \quad (22)$$

where D_0 and Q_D are constants. R is the universal gas constant and T is the absolute temperature. Q_D is sometimes called the apparent activation energy for diffusion. To determine the activation energy at various concentrations, we first show that the calculated mutual diffusion coefficients obey the Arrhenius law. This is shown in figure 6 which is a plot of $\ln D$ against $1/T$. The plots are for concentrations 0.2, 0.4, 0.6, 0.7 and 0.8 atomic fractions of Cd. It can be observed from the figure that Arrhenius relation is obeyed except within and around the concentration range 0.4 to 0.5 atomic fractions of Cd. In this region pronounced deviation from Arrhenius is observed. This is the region where maximum phase segregation and immiscibility has been shown to occur. It can therefore be said that mutual diffusion coefficient may not obey Arrhenius law over a considerably large temperature range within and around concentration ranges where immiscibility or pronounced phase segregation occurs.

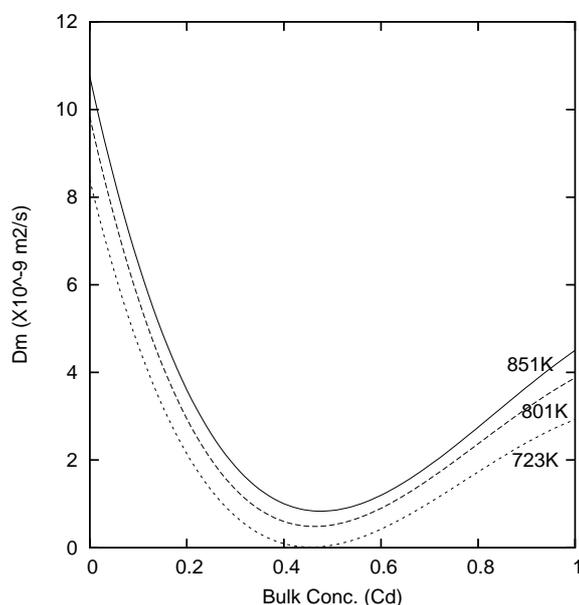


Figure 5. Mutual diffusivities, D_m ($\times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) vs. atomic fraction of Cd for Cd–Ga alloy at the indicated temperatures respectively.

Figure 7 gives a plot of activation energy against the bulk concentration of cadmium. The solid lines represent the average activation energy for Cd–Ga assuming a linear relationship between $\ln D$ and $1/T$ over the temperature range 723 to 851 K. The figure shows that within the region where immiscibility is expected, the activation energy is very high reaching a peak of about 170 kJ/mol. However, within this region we can apply Arrhenius relation averagely in two temperature regions, 723 to 801 K and 801 to 851 K to determine separate activation energy values for the two regions of temperature within the concentration range 0.35 to 0.65 atomic fraction of Cd. The activation energy for the temperature range 723 to 851 K showed very high values peaking at about 220 kJ/mol. Within this temperature range immiscibility is expected. The high activation energy values at these temperatures, which is over ten times higher than normal values will make diffusion processes energetically unfavourable within the affected concentration ranges. On the other hand, as temperature is increased from 801 to 851 K, there is a pronounced reduction in activation energy thereby encouraging diffusion-related activities at higher temperatures within this concentration range. In general, our figures show that high activation energies of diffusion will be associated with regions of phase segregation or immiscibility. Table 3 shows a comparison of values of D_0 for some concentrations especially for concentrations within the region $0.35 \leq c_{\text{Cd}} \leq 0.65$ at different temperature ranges. The values show similar behaviour as the activation energies. The D_0 values for the temperature range 723 to 801 K showed very high values of the order of about 10^5 as against 10^{-6} for the temperature range 801 to 851 K at about 0.45 atomic fraction of Cd.

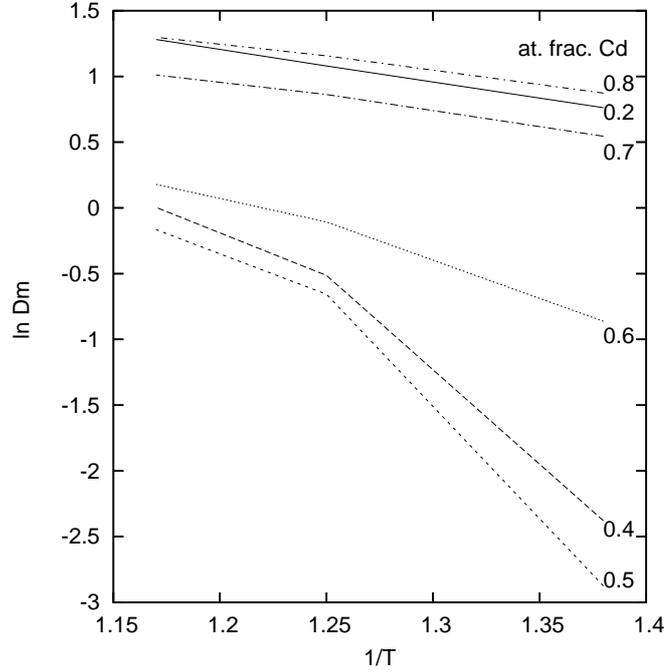


Figure 6. Variation of mutual diffusivities of Cd–Ga liquid alloy with temperature for different compositions of Cd.

3.3 Surface properties

The surface compositions and surface tension values of Cd–Ga liquid alloys were numerically computed from eqs (17) and (18). The activity coefficients for the Cd and Ga atoms at the temperatures of investigation were computed from the expressions in eqs (3) and (4) using the energy parameters given in table 1. 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 (ξ_i) and atomic volume (Ω_i) at the melting temperature of the components of the alloy systems were taken from ref. [7] (where i denotes the components Cd or Ga of the alloy). However, to obtain the surface tension and atomic volume at the working temperatures of 723, 801 and 851 K, the relationship on the temperature dependence of surface tension and atomic volume as given in ref. [24] was used and is given as

$$\xi_i = \xi_{im} + (T - T_m) \frac{\partial \xi_i}{\partial T} \quad (23)$$

and

$$\Omega_i = \Omega_{im} [1 + \theta(T - T_m)], \quad (24)$$

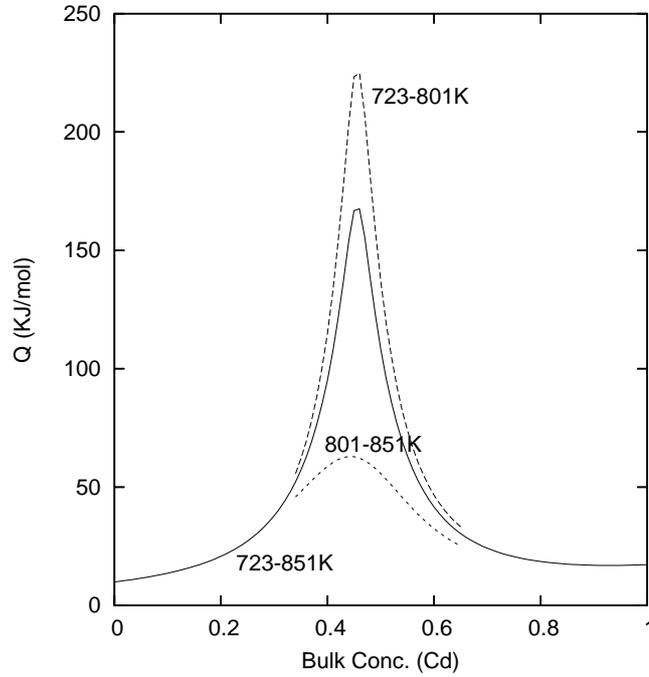


Figure 7. Variation of activation energy for diffusion with bulk concentration of Cd for Cd–Ga liquid alloy at the indicated temperature ranges.

where θ is the thermal coefficient of expansion, Ω_{im} , ξ_{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 $\partial\xi_i/\partial T$ and θ for the pure components of the alloy are obtained from ref. [7]. The atomic surface area α_i for each atomic species of the different alloy systems was calculated using the relation [25]

$$\alpha_i = 1.102 \left(\frac{\Omega_i}{N} \right)^{2/3} \quad (25)$$

and the mean surface area α is then given as

$$\alpha = \sum_i c_i \alpha_i, \quad (26)$$

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

The variation in surface concentration of Cd against its bulk concentration for the three temperatures are shown in figure 8. The plots all have a positive departure from ideality. The figure shows that there are no complete segregation of Cd atoms to the surface but more cadmium atoms are present at the surface than gallium. Cd is known to be very reactive [14], hence its large presence at the surface has far-reaching implications with respect to reactivity with nearby substances. The effect

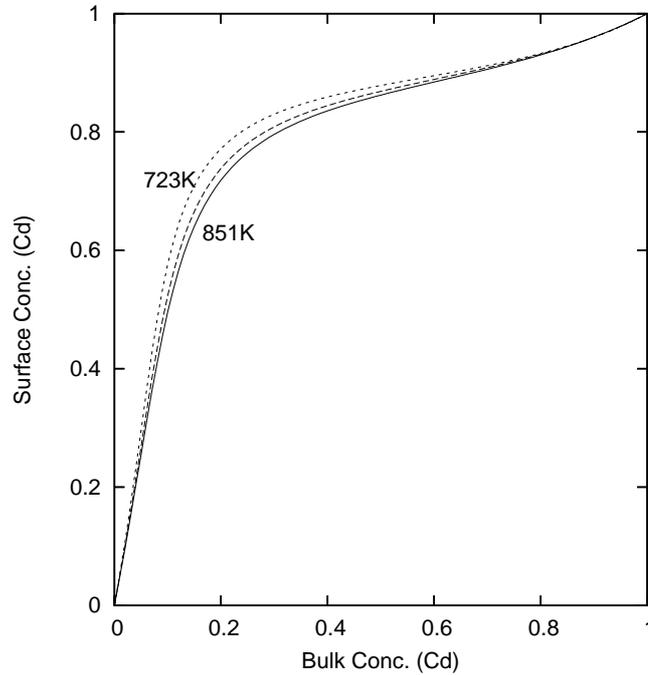


Figure 8. Surface concentration of Cd vs. bulk concentration of Cd for Cd–Ga liquid alloy. Solid lines are values at 851 K, long broken lines are values at 801 K and short broken lines are values at 723 K.

of temperatures on the surface concentration is relatively small decreasing with increasing temperatures and is observed between 0.15 and 0.55 atomic fraction of cadmium. Outside this concentration range, the surface concentration appears invariant with temperatures.

The calculated surface tension values for Cd–Ga at different temperatures are presented in figure 9. There are no experimental values to compare with our calculated results but we mention that calculations using this model had shown reasonable agreement with experiment [6,26]. The figure shows that the surface tension of Cd–Ga liquid alloy generally decrease with increasing temperature throughout the concentration range. There is a pronounced variation in the surface tension values with change in temperature above 0.3 atomic fraction of Cd. At low concentrations of Cd relatively small changes in surface tension are observed for changes in temperature.

In figure 10, the surface $S_{cc}(0)$ shows that strong phase segregation exists at the surface. However, the calculated values do not predict any tendencies to immiscibility at the surface. The surface segregation decreases with increase in temperature. Maximum surface phase segregation is expected to occur around 0.12 atomic fraction of cadmium.

Table 3. Values of D_0 for different temperature ranges across the concentration range $3.5 \leq c_{\text{Cd}} \leq 6.5$.

c_{Cd}	D_0 ($\text{m}^2 \text{s}^{-1}$)		
	723–851 K	723–801 K	801–851 K
0.10	4.44×10^{-8}	–	–
0.20	6.76×10^{-8}	–	–
0.30	3.93×10^{-7}	–	–
0.35	4.42×10^{-6}	9.51×10^{-6}	1.19×10^{-6}
0.40	7.07×10^{-4}	1.93×10^{-2}	4.07×10^{-6}
0.45	1.47×10^1	1.82×10^5	6.11×10^{-6}
0.50	3.77×10^{-3}	4.43×10^{-1}	2.22×10^{-6}
0.55	7.25×10^{-6}	4.41×10^{-5}	4.34×10^{-7}
0.60	4.27×10^{-7}	9.79×10^{-7}	1.17×10^{-7}
0.65	1.10×10^{-7}	1.76×10^{-7}	5.28×10^{-8}
0.70	5.71×10^{-8}	–	–
0.80	3.78×10^{-8}	–	–
0.90	4.02×10^{-8}	–	–

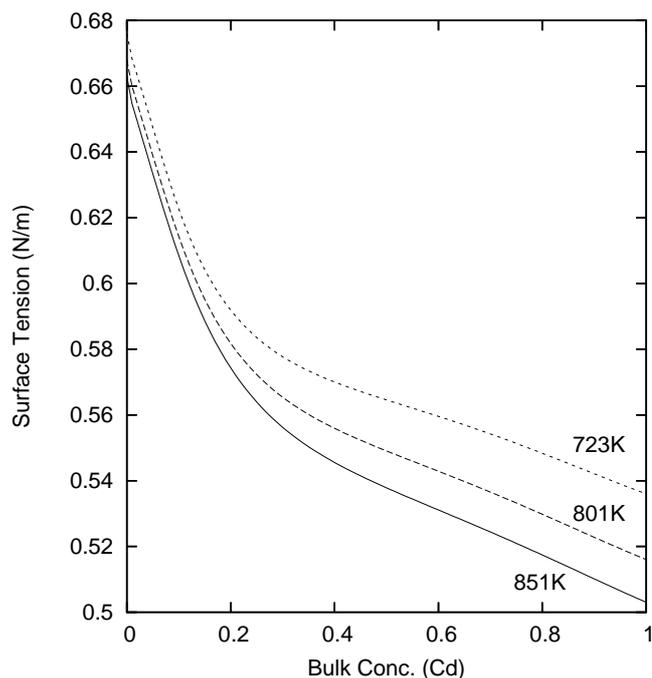


Figure 9. Surface tension vs. bulk concentration of Cd for Cd–Ga liquid alloy at 723, 801 and 851 K.

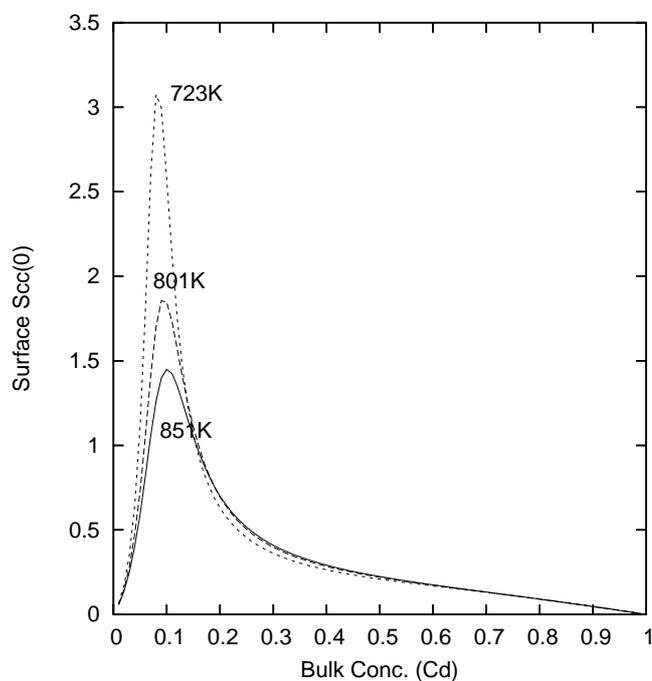


Figure 10. Surface $S_{cc}(0)$ vs. bulk concentration of Cd for Cd–Ga liquid alloy at 723, 801 and 851 K.

4. Conclusion

The Cd–Ga liquid alloy is a strong phase segregating system. The liquid alloy shows tendency to immiscibility between concentrations $0.35 \leq c_{Cd} \leq 0.65$. Within this region, mutual diffusivities of the alloy is very low and approaches zero for temperatures close to 723 K, while the activation energy values are very high peaking at about 220 kJ/mol. Phase segregation in this liquid alloy may affect bulk diffusion processes significantly. However, the effect of bulk segregation on surface related properties are not so pronounced.

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