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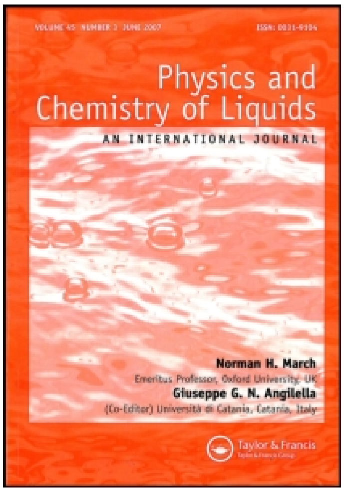

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Influence of strong heterocoordination on surface properties of Li–Pb melts

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The influence of the strong heterocoordination tendency of the Li–Pb liquid alloy on its surface properties has been studied using a statistical thermodynamic model based on compound formation and that based on the layered structure near the interface. In addition to the already proposed saltlike structure Li_4Pb compound formed in the liquid alloy, the study shows that the compound Li_3Pb also has a profound influence on the thermodynamic properties of the liquid alloy. The surface study suggests that the formed compounds in the liquid alloy segregate to the surface about 0.8 atomic fraction of Li. The calculated surface tension of the liquid alloy exhibits a pronounced hump above equiatomic composition.

Keywords: Heterocoordination; Li–Pb liquid alloy; Thermodynamic properties

PACS numbers: 65.70.+y; 28.52.Fa; 61.20.Gy; 61.82.Bg

1. Introduction

Lithium–Lead liquid alloys have attracted the attention of many researchers because of their manifest ‘aggressivity’, which has led to strong deviations of their thermodynamic properties from randomness [1]. The work of Ruppersberg and Eager [2] shows that Li–Pb alloys manifest a preference to an unlike atom arrangement leading to a short-range order in the alloy. At a composition of $x_{\mathrm{Li}} = 0.8$, the liquid alloy exhibits a high peak in its excess stability function values [3]. Other properties of this alloy have been reported to show abnormal behaviour at this composition. For instance, the electrical resistivity of the liquid Li–Pb alloy has a sharp maximum and the thermoelectric power undergoes a change in sign at the mentioned composition [4,5]. The measurement of densities as well as compressibilities of liquid Li–Pb alloys [6] has also shown that the molar volume has a minimum around this composition.

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All these experimental observations tend to support the formation of an ionic compound of saltlike character of the form "Li_4Pb" [6]. As a result it has been observed and mentioned [6] that liquid Li–Pb alloys appear to be constitutively ionic and electrically nonionic. Since this ionic character of the liquid alloy is not unambiguously determined it has also been suggested [6] that other types of bonding may be involved in the compounds formed in this alloy.

Earlier, Zalkin and Ramsey [7] have identified four compounds within the vicinity of 0.8 atomic fraction of lithium in the Li–Pb liquid alloy. These compounds are indicated in the phase diagrams of Li–Pb alloy given in [8] and are $Li_{22}Pb_5$, Li_7Pb_2, Li_3Pb and Li_8Pb_3. Surprisingly, Zalkin and Ramsey did not mention any compound of the form Li_4Pb. This could in a way support the view that bonding between lithium and lead is not purely ionic and could involve other kinds of bonding. This view will make room for the formation and existence of these aforementioned compounds. However, it can be said that among all the compounds identified and suggested for the liquid Li–Pb alloy, probably only those compounds that dominate in their number density could effectively influence the properties of the liquid alloy.

To understand how these identified and suggested compounds influence the thermodynamic properties of the Li–Pb alloy, a statistical thermodynamic model based on compound formation [9], which had successfully been applied to Li–Mg liquid alloy [10], will be used to calculate the thermodynamic properties including the concentration–concentration fluctuation at the long wavelength limit, $S_{cc}(0)$, of the Li–Pb liquid alloy based on the configurations of the different identified and suggested compounds already mentioned above. This will go a long way to suggest the probable compounds among all mentioned above that will have a marked influence on the thermodynamic properties of the liquid Li–Pb alloy and on the other hand give more insight into the kind of bonding present in the liquid alloy.

Incidentally, thermodynamic properties of liquid binary alloys have been related to their surface properties. The statistical formulations of Prasad *et al.* [11] based on the concept of layered structure near the interface for the determination of surface properties gave a valuable link between surface properties and bulk thermodynamic properties of a liquid binary alloy. Interestingly, this formulation determines surface properties not from energetics and factors based on geometry only but also has as input valuable thermodynamic data, such as the activity coefficients of the alloy components in the bulk. The obvious implication is that it is possible to observe the effect of bulk thermodynamic properties influenced by heterocoordination tendencies on the surface properties of a liquid binary alloy.

In this work therefore, the recent experimental work of Gasior and Moser [12] was used to obtain the experimental thermodynamic data, which served as a guide for the calculated values. In the next section, the basic expressions of the statistical models are outlined and the results of the calculation are given in section 3, while the conclusions are given in section 4.

2. Theoretical models

The statistical model based on compound formation uses the idea that the thermodynamic properties of a compound forming A–B alloy can be explained by treating the alloy as a pseudo ternary mixture of A atoms, B atoms and $A_\mu B_\nu$ complexes. Details of the formulation are given in [9].

The thermodynamic properties of interest include the Gibbs free energy of mixing, entropy of mixing and activity of the metal in the liquid alloy. The Gibbs free energy of mixing is obtained from the expression,

$$G_{\mathrm{m}} = G_{\mathrm{m}}^{\mathrm{es}} + RT[x \ln x + (1-x)\ln(1-x)]. \tag{1}$$

Here, x is the concentration of atom A, R is the universal gas constant and $G_{\mathrm{m}}^{\mathrm{es}}$ is the excess free energy of mixing and its expression in the compound formation model is given as,

$$\frac{G_{\mathrm{m}}^{\mathrm{es}}}{RT} = z\int_o^x \left[\ln\sigma + (2kT)^{-1}(P_{aa}\Delta\epsilon_{aa} - P_{bb}\Delta\epsilon_{bb})\right]\mathrm{d}x + \psi \tag{2}$$

where z is the co-ordination number, k the Boltzman constant and $\Delta\epsilon_{ij}$ is the change in energy if the $i-j$ bond is in the complex $A_\mu B_\nu$. P_{ij} denotes the probability that the bond is part of the complex. The expressions for P_{ij} and $\ln\sigma$ are already given in literature [9]. The constant ψ is determined from the requirement that $G_{\mathrm{m}}=0$ at $x=1$.

The entropy of mixing S_{m} is obtained from the equation

$$S_{\mathrm{m}} = -(\partial G_{\mathrm{m}}/\partial T)_p \tag{3}$$

and the activities of the metals are obtained from the expression

$$a_{\mathrm{m}} = x\gamma_{\mathrm{m}} \tag{4}$$

where x is the concentration of the species and γ_{m} is its activity coefficient given by

$$\gamma_{\mathrm{m}} = \left\{\frac{\beta - 1 + 2x}{x(1+\beta)}\right\}^{(1/2)z}. \tag{5}$$

The expression for β is already given in [9] and the detailed expression for entropy of mixing under the compound formation model has been given in [13].

The concentration–concentration fluctuations $S_{\mathrm{cc}}(0)$ in the long wavelength limit have been shown [9] to be given by

$$S_{\mathrm{cc}}(0) = x(1-x)\left\{1 + \frac{1}{2}z\left(\frac{1}{\beta} - 1\right) + \Omega\right\}^{-1} \tag{6}$$

where Ω is the expression given below:

$$\Omega = \frac{zx(1-x)}{2\beta kT}\Theta \tag{7}$$

and

$$\Theta = \left[2(1-2x)P'_{ab}\Delta\epsilon_{ab} + (\beta - 1 + 2x)P'_{aa}\Delta\epsilon_{aa} - (\beta + 1 - 2x)P'_{bb}\Delta\epsilon_{bb}\right] \tag{8}$$

where the prime on P denotes the first derivative with respect to x.

A statistical mechanical model, which is derived from the concept of a layered structure near the interface was used by Prasad and Singh [14] and Prasad *et al.* [11] to obtain expressions for surface properties. The surface grand partition function Ξ^s is related to the surface tension ζ by the expression

$$\Xi^s = \exp\left(\frac{-A\zeta}{kT}\right) = \exp\left(\frac{-N^s\zeta\xi}{kT}\right) \tag{9}$$

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

Prasad *et al.* [11] gave the expression for surface tension of the binary alloys in terms of the activity coefficient of the alloy components as

$$\zeta = \zeta_A + \frac{kT}{\xi}\ln\frac{x_A^s}{x_A} - \frac{kT}{\xi}\ln\gamma_A + \left[p(x_B^s)^2 + q(x_B)^2\right]\frac{w}{\xi} \tag{10}$$

$$\zeta = \zeta_B + \frac{kT}{\xi}\ln\frac{x_B^s}{x_B} - \frac{kT}{\xi}\ln\gamma_B + \left[p(x_A^s)^2 + q(x_A)^2\right]\frac{w}{\xi} \tag{11}$$

where ζ_A and ζ_B are surface tension values for the pure components A and B respectively. x_i and x_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, w is the interchange energy, p and q are known as the surface coordination fractions. The expressions for the surface tension without the activity coefficients of the alloy components were obtained by Prasad and Singh [14] and are given as

$$\zeta = \zeta_A + \frac{kT}{\xi}\ln\frac{x_A^s}{x_A} + \left[p(x_B^s)^2 - (p+q)(x_B)^2\right]\frac{w}{\xi} \tag{12}$$

$$\zeta = \zeta_B + \frac{kT}{\xi}\ln\frac{x_B^s}{x_B} + \left[p(x_A^s)^2 - (p+q)(x_A)^2\right]\frac{w}{\xi} \tag{13}$$

where all symbols retain their meaning as already defined above. The surface $S_{cc}(0)$ can be written as [11]

$$S_{cc}^s(0) = x_A^s x_B^s\left[1 + \left(\frac{z^s}{2\beta^s}\right)(1-\beta^s)\right]^{-1} \tag{14}$$

where

$$\beta^s = \left\{1 + 4x_A^s x_B^s\left[\exp\left(\frac{2w}{z^s kT}\right) - 1\right]\right\}^{1/2}. \tag{15}$$

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 statistical mechanical model based on compound formation was applied to the Li–Pb liquid alloys to determine the activity of Li, integral Gibbs free energy of mixing and entropy of mixing values. The expressions used for these calculations are already given in the previous section. Our interest is to determine which of the identified or suggested compounds for the Li–Pb liquid alloy could reproduce the known thermodynamic properties of the alloy. To achieve this we assume that the Li–Pb liquid alloy forms each of these compounds already mentioned in turn. In this case we take the compound formed in the liquid Li–Pb alloy to be $\mathrm{Li}_{\mu}\mathrm{Pb}_{\nu}$, which is of the form $\mathrm{A}_{\mu}\mathrm{B}_{\nu}$. For each compound μ and ν are picked based on the configuration of the compound under consideration. Once μ and ν are picked and fixed for a particular compound, the equations for activity, free energy of mixing and entropy are solved and the interaction parameters w, $\Delta\epsilon_{ab}$, $\Delta\epsilon_{aa}$, $\Delta\epsilon_{bb}$ and their derivatives $\partial w/\partial T$, $\partial\Delta\epsilon_{ab}/\partial T$, $\partial\Delta\epsilon_{aa}/\partial T$ and $\partial\Delta\epsilon_{bb}/\partial T$ were fine-tuned such that they reproduce simultaneously and to a reasonable degree of accuracy the experimental activity of Li, the integral Gibbs free energy of mixing and entropy values for the Li–Pb liquid alloy.

For the compounds $\mathrm{Li}_{22}\mathrm{Pb}_{5}$, $\mathrm{Li}_{7}\mathrm{Pb}_{2}$ and $\mathrm{Li}_{8}\mathrm{Pb}_{3}$ with μ and ν being 22 and 5, 7 and 2, 8 and 3 respectively, it is reported that there were no sets of values of interaction parameters that could reproduce the experimental values of activity of Li, integral Gibbs free energy of mixing and entropy of mixing reasonably and simultaneously. Hence, we conclude that for these compounds, their individual presence in the Li–Pb liquid alloy has negligible influence on the thermodynamic properties of the alloy.

Figure 1 gives the comparison between the calculated activity of Li with the experimental values. The solid lines are calculated values when the compound $\mathrm{Li}_{4}\mathrm{Pb}$ was considered and broken lines are the calculated values when the compound $\mathrm{Li}_{3}\mathrm{Pb}$ was considered. The points are experimental values at 878 K obtained from [12]. The values of μ, ν and the interaction parameters for this calculation are given in table 1. It is obvious from the figure that both compounds reproduced a qualitative trend of the activity. The main deviations from the experiment occurred between 0.6 and 0.85 atomic fraction of Li. However, the compound $\mathrm{Li}_{3}\mathrm{Pb}$ had a closer fit for the experimental activity data.

Figures 2 and 3 show the comparison of the calculated integral Gibbs free energy of mixing and entropy of mixing with the experiment respectively. The points represent experimental values for the Gibbs free energy of mixing [12] and entropy of mixing [15] respectively. The calculated values for the two compounds show reasonable agreement with the experiment. In the case of the free energy of mixing, the $\mathrm{Li}_{4}\mathrm{Pb}$ compound showed better agreement about 0.8 atomic fraction of Li. The calculated entropy values for $\mathrm{Li}_{4}\mathrm{Pb}$ showed a minimum at about 0.8 atomic fraction of Li while that for the compound $\mathrm{Li}_{3}\mathrm{Pb}$ showed a minimum at about 0.6 atomic fraction of Li.

Figure 4 compares the $S_{\mathrm{cc}}(0)$ values obtained using the configuration of the two compounds $\mathrm{Li}_{4}\mathrm{Pb}$ and $\mathrm{Li}_{3}\mathrm{Pb}$ with the experimental values. The experimental values of the $S_{\mathrm{cc}}(0)$ were obtained by Gasior and Moser [12] from excess stability values. Here also both compounds reproduced a qualitative trend of the $S_{\mathrm{cc}}(0)$, however, the compound

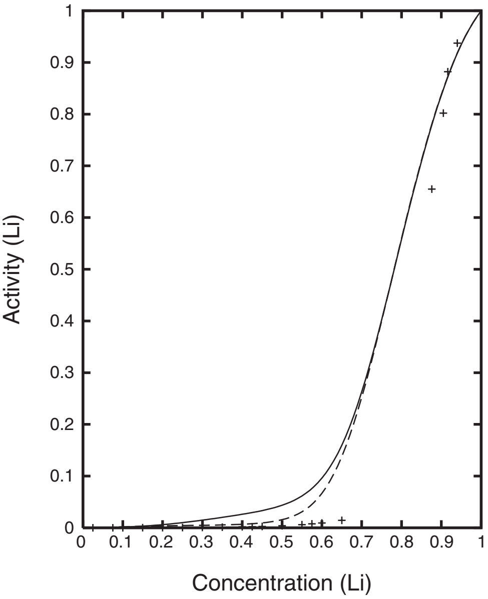

Figure 1. Activity *vs.* bulk concentration of Li for Li–Pb liquid alloy. Solid line represents calculated activity values for Li_4Pb. Broken line represents calculated activity values for Li_3Pb. Points represent experimental activity values for Li at 878 K.

Table 1. Interaction parameters used for compounds Li_4Pb and Li_3Pb in liquid Li–Pb alloys.

	μ	ν	$\frac{w}{kT}$	$\frac{\Delta\epsilon_{ab}}{kT}$	$\frac{\Delta\epsilon_{aa}}{kT}$	$\frac{\Delta\epsilon_{bb}}{kT}$	$\left(\frac{1}{kT}\right)\frac{\partial w}{\partial T}$ (K^{-1}) ($\times10^{-4}$)	$\left(\frac{1}{kT}\right)\frac{\partial\Delta\epsilon_{ab}}{\partial T}$ (K^{-1}) ($\times10^{-4}$)	$\left(\frac{1}{kT}\right)\frac{\partial\Delta\epsilon_{aa}}{\partial T}$ (K^{-1}) ($\times10^{-4}$)	$\left(\frac{1}{kT}\right)\frac{\partial\Delta\epsilon_{bb}}{\partial T}$ (K^{-1})
Li_4Pb	4	1	−4.98	−1.69	−0.99	0.00	100.0	−1.00	54.00	0.00
Li_3Pb	3	1	−4.41	−0.35	−0.08	0.00	120.0	−7.30	35.00	0.00

Li_4Pb produced a curve that fits better the experimental value producing a minimum close to 0.8 atomic fraction of Li. On the other hand, using the configuration of the Li_3Pb compound, the calculated $S_{cc}(0)$ shows a minimum at about 0.6 atomic fraction of Li.

From the above results, it is obvious that Li–Pb liquid alloy has a strong tendency to heterocoordination. The possible compounds that could reproduce its thermodynamic properties to a reasonable extent are Li_4Pb and Li_3Pb. Though the compound Li_4Pb in general reproduced the thermodynamic properties of the Li–Pb liquid alloy better exhibiting a very close fit about the 0.8 atomic fraction of Li, the compound Li_3Pb also has a pronounced influence on these thermodynamic properties. The ability of the compound Li_3Pb to reproduce to a reasonable extent the manifest properties of this alloy suggests its pronounced presence in the liquid. This in a way has lent support to the view that the compound formation in Li–Pb alloy is not purely ionic and that other kinds of bonding may be involved [6]. We comment here that in addition to the saltlike structure Li_4Pb being suspected, the compound Li_3Pb could also be prevalent enough in the Li–Pb alloy to influence its properties and its bonding type

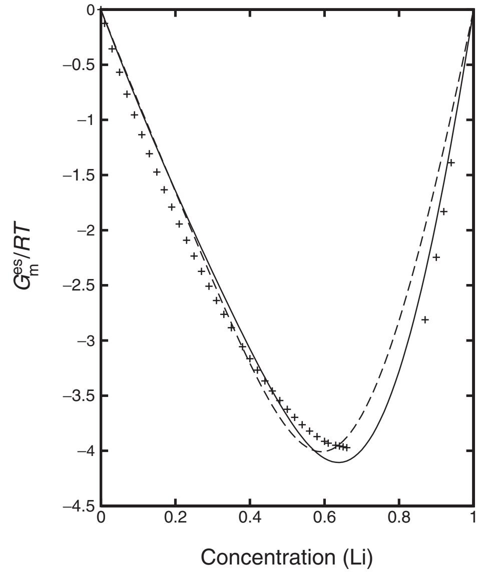

Figure 2. Integral G_m^{es}/RT *vs.* bulk concentration of Li for Li–Pb liquid alloy. Solid line represents calculated values for Li_4Pb. Broken line represents calculated values for Li_3Pb. Points represent experimental values at 878 K.

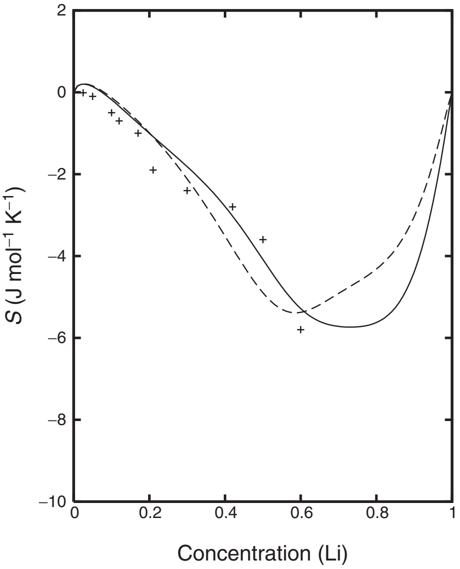

Figure 3. Entropy of mixing *vs.* bulk concentration of Li for Li–Pb liquid alloys. Solid line represents calculated values for Li_4Pb. Broken line represents calculated values for Li_3Pb. Points represent experimental values at 873 K.

may not be ionic. The other compounds $Li_{22}Pb_5$, Li_8Pb_3 and Li_7Pb_2 will be present but perhaps in trace quantities.

To study the effect of this strong heterocoordination tendency of Li–Pb liquid alloy on its surface properties, we employ the expressions due to Prasad and Singh [14] given

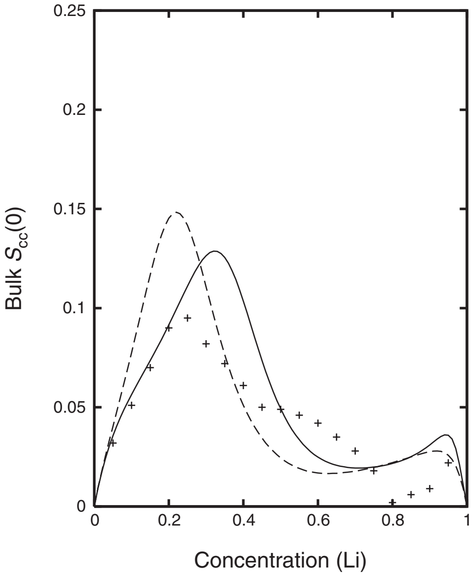

Figure 4. Bulk $S_{cc}(0)$ *vs*. bulk concentration of Li for Li–Pb liquid alloy. Solid line represents calculated values for Li_4Pb. Broken line represents calculated values for Li_3Pb. Points represent experimental values. Dots are ideal values.

in equations (12) and (13). These expressions help us to determine surface properties when the activity coefficients of the liquid alloy components are not used in the calculations. The expressions due to Prasad *et al.* [11] in equations (10) and (11) are now used to compute the same surface properties, in this case, including the activity coefficients. In this way the effect of the strong compound-forming tendency of this alloy will be easily observed. The activity coefficients for Li and Pb atoms were computed from the expressions in equation (5) using the energy parameters given in table 1. The surface coordination fractions p and q are taken as those for close packed structures with $p=0.5$ and $q=0.25$. The surface tension (ζ_i) and atomic volume (Ω_i) at the melting temperatures of the components of the alloy system were taken from [16] (where i denotes Li or Pb). However, to obtain the surface tension and atomic volumes at the working temperature of 878 K, the relationship of the temperature dependence of surface tension and atomic volumes of liquid metals was used as given in [17];

$$\zeta_i = \zeta_{im} + (T - T_{\mathrm{m}})\frac{\partial \zeta_i}{\partial T} \tag{16}$$

and

$$\Omega_i = \Omega_{im}[1 + \theta(T - T_{\mathrm{m}})] \tag{17}$$

where θ is the thermal coefficient of expansion, Ω_{im}, 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 kelvin. The values of $\partial\zeta_i/\partial T$ and θ for the pure alloy components were obtained from [16]. The atomic surface area ξ_i for each atomic species of the different alloy systems was calculated following the relation [18]

$$\xi_i = 1.102\left(\frac{\Omega_i}{N}\right)^{2/3} \tag{18}$$

and the mean surface area ξ is then given as

$$\xi = \sum_i x_i \xi_i \tag{19}$$

where N is the Avogadro number and x_i are the concentrations of the alloy components.

Figure 5 shows the plot of surface concentration of Li against its bulk concentration using the activity coefficients calculated by considering the configuration of the two compounds Li_4Pb and Li_3Pb. The solid lines represent values due to the compound Li_4Pb, the long broken lines show values due to Li_3Pb and the short broken lines show calculated values when activity coefficients were not considered. The curves obtained due to the compounds have similar trends except that the line due to Li_3Pb appears deeper about 0.4 bulk atomic concentration of Li. However, about 0.8 ± 0.1 bulk atomic fraction of Li, the curves indicate complete segregation of atoms to the surface. This is in contrast to our calculations when the activity coefficients are not considered. This segregation must be an effect of the strong heterocoordination tendency about this composition range.

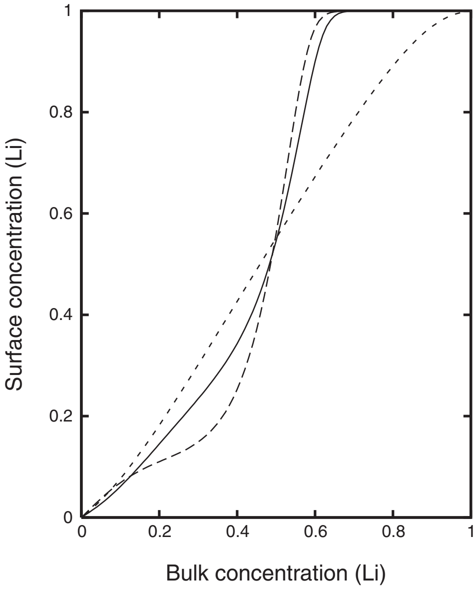

Figure 5. Surface concentration *vs.* bulk concentration of Li for Li–Pb liquid alloy. Solid line represents calculated values for Li_4Pb. Long broken line represents calculated values for Li_3Pb. Short broken line represents calculated values when activity coefficient values were not considered.

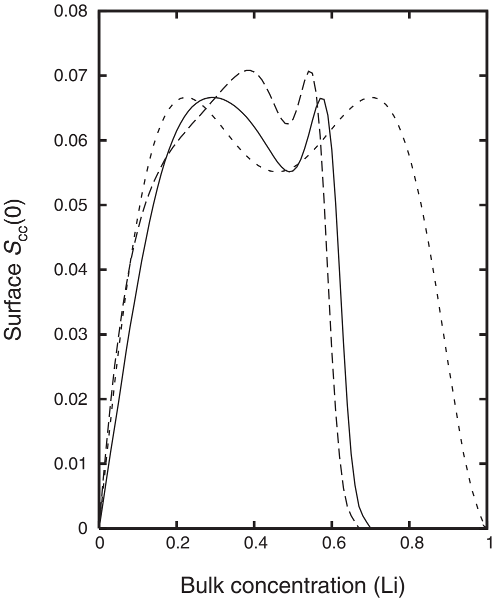

Figure 6. Surface concentration fluctuation ($S^{s}_{cc}(0)$) *vs.* bulk concentration of Li for Li–Pb liquid alloys. Solid line represents calculated values for Li_4Pb. Long broken line represents calculated values for Li_3Pb. Short broken line represents calculated values when the activity coefficient values were not considered.

The variation of the surface concentration–concentration fluctuation at the long wavelength limit $S^{s}_{cc}(0)$ with bulk concentration of Li is shown in figure 6. It can be noticed that when the compounds Li_4Pb and Li_3Pb are considered in the calculation, the surface $S^{s}_{cc}(0)$ indicates full compound formation within the mentioned region of about 0.8 bulk atomic fraction of Li. It can be reasoned that in this region where compound formation appears to be maximum, the formed compounds do not remain in the mix but segregate to the surface. We recall that about this region of concentration the liquid Li–Pb alloy is being considered for a blanket material for controlled nuclear fusion [12,19].

Figure 7 gives the surface tension of liquid Li–Pb alloys as a function of the bulk concentration. There are no experimental values of surface tension for this alloy to guide our calculations. However, the influence of strong heterocoordination on the surface tension of this alloy can be seen when the calculated surface tension considering the formed compounds is compared with calculated values of surface tension not based on the activity coefficients. The pronounced hump which occurred after the equiatomic composition must be a manifest effect of strong heterocoordination tendency of the alloy. Though our calculations did not indicate the hump very close to 0.8 atomic fraction of Li, we believe that the calculated values will give a reasonable trend of the experimental surface tension values.

4. Conclusion

The compounds Li_4Pb and Li_3Pb appear to dominate the behaviour of the thermodynamic properties of the liquid Li–Pb alloy. The heavy presence of these compounds

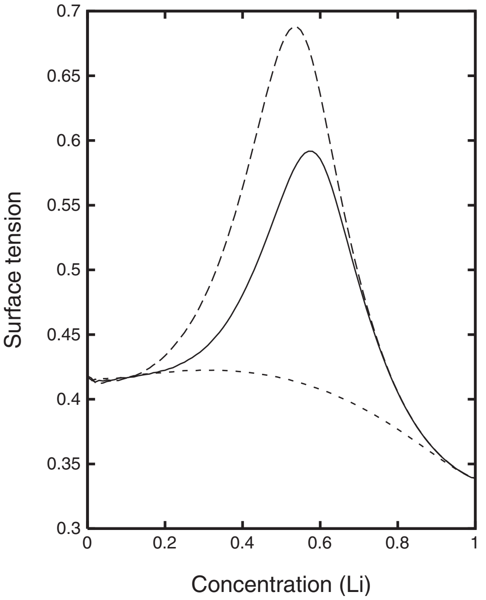

Figure 7. Surface tension *vs.* bulk concentration of Li for Li–Pb liquid alloy. Solid line represents calculated values for Li_4Pb. Long broken line represents calculated values for Li_3Pb. Short broken line represents calculated values when the activity coefficient values were not considered.

leads to a pronounced effect on the surface properties of the liquid alloy and suggests a surface segregation of the formed compounds at high lithium concentration.

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