ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Free Energy of Mixing of Two Lead Based Binary Liquid Alloys

RN Yadav and SK Chakrabarti*

Dept. of Mathematics and *Dept. of Physics, M. M. A. M. Campus, Biratnagar, Tribhuvan University, Nepal.

ABSTRACT

There are a large number of binary liquid alloys which exhibit interesting behaviour as a function of concentration as regards the thermodynamic properties. In the present work we have considered two binary molten alloys of lead—Li-Pb and Na-Pb—and tried to calculate their free energy of mixing at different concentrations of the ingredients. The former alloy shows asymmetry in its free energy of mixing (G_M) whereas in case of the latter G_M is symmetric around the equi-atomic composition. Flory's model has been applied to study such thermodynamic behaviour of them. It is a statistical mechanical model based on the size factor of the constituent species of binary molten alloys. For each alloy we have started with the mathematical expression for the activity of some metal within it according to this model. Activity (a) is one of the fortunate thermodynamic functions which are obtained directly from experiment. After knowing the ratio of the atomic volumes of the constituent species of the alloy the prime task becomes the determination of the interchange energy between them. For this purpose the experimental values of 'a' for different concentrations of an ingredient are collected. From these known values interchange energy ( )has been computed by using the expression for 'a'. A suitable value of is chosen from the set of values so obtained. Putting this value of the activity is calculated for several concentrations and then compared with its observed values. Accordingly, a modified value of has been considered and the calculations are repeated. In this way by the method of successive approximations we have ascertained the value of the interchange energy. Thereafter G_M has been computed from the mathematical expression of it according to the said model. The results explain the observed anomaly as well as symmetry in the free energy of mixing of the present liquid alloys.

Key words: Binary liquid alloys, Flory's model, Activity, Free energy of mixing.

Corresponding author
Email: skc_2007@yahoo.com

ISSN: 0975-8585

INTRODUCTION

The concentration dependent thermodynamic and electrical properties of binary liquid alloys, especially the complex forming ones, are interesting in many ways. The properties of mixing are not symmetrical about the equi-atomic composition—deviating maximally from that of the ideal alloys. Some of these alloys also depict metal-nonmetal transition across a narrow band of concentrations. The liquidus lines are usually S-shaped and the heat of mixing and excess free energy of mixing are large negative quantities at one or other concentrations [1–3]. The anomalous behaviour of these liquid alloys is least understood and demands extensive theoretical investigation [4–7].

The alloying behaviour of liquid alloys can be studied by the help of two distinct theories *e.g.* electronic theory of mixing and statistical mechanical theory of mixing. According to the first theory a liquid alloy is assumed to consist of a system of ions and electrons. The problem, usually, in this approach is tackled through pseudo-potential theory [8, 9] and hard sphere model [10–13]. But they cannot be used to obtain information regarding the concentration fluctuations in the long wave-length limit [$S_{cc}(0)$], an important thermodynamic function which determines the stability of alloys. The conformal solution model [14] has been used by many theoreticians to study $S_{cc}(0)$ of different binary alloys [15, 16]. But this model cannot be used to study the short-range order parameters. However, in the eighty's decade soft sphere model [17] and one-component plasma theory [18] came into being for the binary liquid alloys to supplement the electronic theory of mixing. But the approach as a whole is found to be suitable for explaining mainly the electrical properties of alloys. On the other hand, the statistical mechanical theory of mixing can be successfully used to obtain the analytical expressions for various thermodynamic functions.

In the present work two binary liquid alloys of lead have been considered *e.g.* Li-Pb and Na-Pb. The liquidus lines of these alloys reveal that the constituent species form complexes. We have considered Flory's model [19] for computation of their free energy of mixing. It is a statistical mechanical model for the binary molten alloys in which the size factor of the constituent species is taken into account.

In Section 2 the working expression according to this model is furnished. Section 3 deals with the results of computation for the free energy of mixing of these complex forming binary liquid alloys of lead. Section 4 provides a brief conclusion.

FORMULATION

Activity is one of the fortunate thermodynamic functions which are obtained directly from experiment. Activity of an element in a binary liquid alloy is given by

$$K_B T \ln a = -zFE,$$

ISSN: 0975-8585

where 'z' is the valency of carrier ions of the element, F the Faraday's constant, K_B the Boltzmann constant, T the absolute temperature and E the electromotive force which is observed directly from the experiment.

According to Flory's model the activity (a) of a metal within a binary liquid alloy :

$$\ln a = \ln \frac{c(1-\upsilon)}{1-\upsilon c} + \frac{\upsilon(1-c)}{1-\upsilon c} + \frac{\omega}{RT}\frac{(1-c)^2}{(1-\upsilon c)^2}, \quad (1)$$

where

$$\upsilon = 1 - \frac{V_A}{V_B}, \quad (2)$$

V_A and V_B being the atomic volumes of species A and B respectively.

Now, let us recall the standard thermodynamic relation

$$RT \ln a = G_M + (1-c)\frac{\partial G_M}{\partial c}, \quad (3)$$

where R is the universal gas constant and 'c' the concentration of the element within the mixture.

Putting in (3) the expression for ln a from (1) and solving for G_M we get the expression for the free energy of mixing of a binary liquid alloy :

$$G_M = RT\,[c\ln c + (1-c)\ln(1-c) + c\ln(1-\upsilon) - \ln(1-\upsilon c)] + \omega c\frac{1-c}{1-\upsilon c}. \quad (4)$$

RESULTS AND DISCUSSION

Lithium-Lead Liquid Alloy

For the lithium-lead liquid alloy

$$A \equiv Li, \qquad B \equiv Pb.$$

Knowing the ratio of the atomic volumes of lithium and lead [20] *i.e.*

$$\frac{V_A}{V_B} = 0.7167$$

we have from (2)

$$\upsilon = 0.2833.$$

The value of the interchange energy (ω) has been ascertained from the experimental values of the activity of lithium within the liquid alloy at 932 K. [5] by the method of successive approximations :

$$\frac{\omega}{RT} = -8.7.$$

ISSN: 0975-8585

The computed values of the free energy of mixing (G_M/RT) of Li-Pb liquid alloys at 932 K. are furnished in Table–1 along with its observed values [5] in the concentration range of lithium from 0.1 to 0.9.

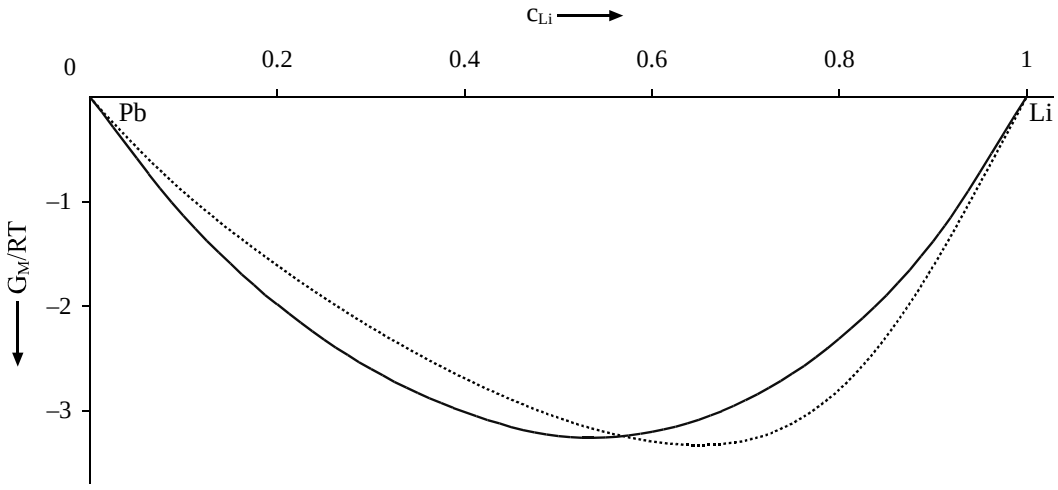
Table–1: FREE ENERGY OF MIXING
of Li-Pb liquid alloys at 932 K.

c_{Li}	G_M/RT	
	Theoretical	**Experimental***
0.1	–1.1355	–0.921
0.2	–1.9843	–1.605
0.3	–2.6008	–2.200
0.4	–3.0129	–2.700
0.5	–3.2409	–3.078
0.6	–3.2022	–3.276
0.7	–2.9019	–3.274
0.8	–2.3098	–2.806
0.9	–1.3815	–1.597

*Saboungi et al, 1978

The plot of G_M/RT versus c_{Li} is depicted in Figure–1 for both the theoretical and experimental values. The computed and observed values of the free energy of mixing are in reasonable agreement. The observed values of G_M are slightly greater than the computed values for $c_{Li} < 0.58$ and in the concentration range $c_{Li} > 0.58$ the theoretical values are slightly greater than the experimental ones. The experimental value of the free energy of mixing is minimum at $c_{Li} = 0.65$ while the computed value of it is minimum at $c_{Li} = 0.54$. Thus the asymmetry in the values of G_M for Li-Pb liquid alloys is well explained.

Figure–1
G_M/RT–c_{Li} Graph



ISSN: 0975-8585

Figure–1 : Free energy of mixing (G_M/RT) of Li-Pb liquid alloy at 932 K. for different concentrations of lithium. The full curve represents the theoretical values. The dotted curve shows the experimental values due to Saboungi *et al* (1978).

Sodium-Lead Liquid Alloy

In case of sodium-lead liquid alloy

$$A \equiv Na, \qquad B \equiv Pb.$$

Knowing the ratio of the atomic volumes of sodium and lead at 700 K. [21] *i.e.*

$$\frac{V_A}{V_B} = 1.3918$$

we have from (2)

$$\upsilon = -0.3918.$$

The value of the interchange energy (ω) has been found out from the experimental values of the activity of lead within the liquid alloy at 700 K. [21] by the method of successive approximations :

$$\frac{\omega}{RT} = -10.$$

The computed values of the free energy of mixing (G_M/RT) of Na-Pb liquid alloys at 700 K. are tabulated in Table–2 along with its experimental values [21] in the concentration range of lead from 0.1 to 0.9.

Table–2: FREE ENERGY OF MIXING
of Na-Pb liquid alloys at 700 K.

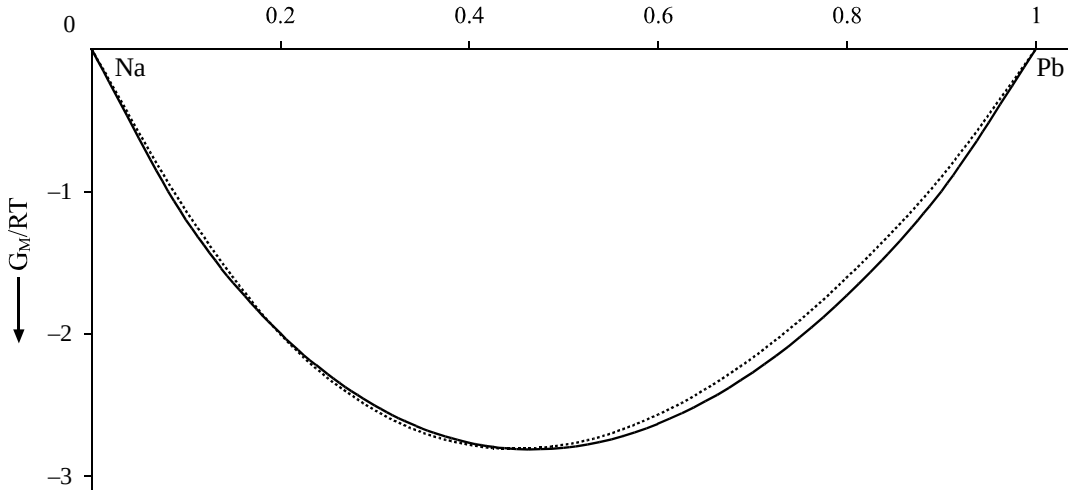
c_{Pb}	G_M/RT	
	Theoretical	**Experimental***
0.1	–1.1965	–1.132
0.2	–1.9935	–1.999
0.3	–2.5019	–2.535
0.4	–2.7612	–2.776
0.5	–2.7972	–2.777
0.6	–2.6290	–2.564
0.7	–2.2698	–2.166
0.8	–1.7268	–1.602
0.9	–0.9950	–0.895

*Hultgren *et al*, 1973

ISSN: 0975-8585

The plot of G_M/RT versus c_{Pb} is furnished in Figure–2 for both the computed and observed values. The theoretical and experimental values of the free energy of mixing are in good agreement. The computed value of the free energy of mixing is minimum at c_{Pb} = 0.47 while experimentally it is found to be minimum at c_{Pb} = 0.5. Thus the symmetry in the values of G_M around equi-atomic composition for Na-Pb liquid alloys is explained well by this model.

Figure–2
G_M/RT–c_{Pb} Graph



Figure–2 : Free energy of mixing (G_M/RT) of Na-Pb liquid alloy at 700 K. for different concentrations of lead. The full curve represents the theoretical values. The dotted curve shows the experimental values due to Hultgren *et al* (1973).

CONCLUSION

The anomaly in the free energy of mixing (G_M) of lithium-lead liquid alloys is well explained by the present theoretical model. The symmetry in G_M around equi-atomic composition in case of sodium-lead liquid alloys is also explained nicely by this model. The nature of curves as found experimentally is corroborated to a great extent by the computed values of free energy of mixing for these complex forming binary liquid alloys of lead for different concentrations of the ingredients.

REFERENCES

[1] P Chieux and H Ruppersberg, J Phys. (Les Ulis. Fr.) C 8 (Lam 4) 41, 145 (1980)
[2] P Lamparter, W Martin and S Steeb, J. Non-Cryst. Solids. 61, 279 (1984)
[3] C N Wagner, J. Rap. Quen. Met. B V, 405 (1985)
[4] V A Roeder and W Morawietz, Z. Metallude. 47, 734 (1956)

[5] M L Saboungi, J Marr and M Blander, J. Chem. Phys. 68, 1375 (1978)
[6] S M Osman and R N Singh, Phys. Rev. E 51, 332 (1995)
[7] S K Chakrabarti, I S Jha, R P Yadav and B P Singh, Orissa J. Phys. 17, 153 (2010)
[8] W A Harrison, Pseudopotential in the theory of metals (Benjamin, New York, 1966)
[9] V Heine, Solid state physics (Academic, New York, 1970)
[10] E Theile, J. Chem. Phys. Lett. 39, 474 (1963)
[11] J L Lebowitz, Phys. Rev. AL 33, 895 (1964)
[12] T E Faber, Introduction to the theory of liquid metals (Cambridge Univ. Press, Cambridge, 1972)
[13] M Shimoji, Liquid metals (London Acad., London, 1977)
[14] H C Longuet-Higgins, Proc. Roy. Soc. A 205, 247 (1951)
[15] A B Bhatia, W H Hargrove and N H March, J. Phys. C 6, 621 (1973)
[16] J A Alonso and N H March, Physica, B 114, 67 (1982)
[17] B Bernu, J P Hansen, Y Hiwatari and G Pastore, Phys. Rev. A 36, 4891 (1987)
[18] W Li and M P Tosi, Il Nuovo Cim. 11, 1509 (1989)
[19] P J Flory, J. Chem. Phys. 10, 51 (1942)
[20] P C Rakshit and A Das, Organic Chemistry (Sc. Book Agency, Kolkata, 1973)
[21] R Hultgren, P D Desai, D T Hawkins, M Gleiser and K K Kelley, Selected values of the thermodynamic properties of binary alloys (A. S. M., Ohio, 1973)