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ARTICLE

Calculation of Excess Stability Functions of Four Binary Alloys

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Abstract: The thermodynamic model based on cluster of two atoms is considered with the view to obtaining Scc(0) and the excess stability function of Scc(0). Concentration-concentration fluctuation; Scc(0) of four binary molten alloys was calculated. The thermodynamic properties of these alloys are evaluated based on cluster of two atoms (A & B) or (B & A). Each system has the view of obtaining concentration-concentration fluctuation; Scc(0) enumerating the low-order atomic correlation in the nearest neighbour shell of liquid binary alloys.The highlights of excess stability functions(ES) of Scc(0) of these alloys were reported. The values of Scc(0) for all these alloys are higher than the ideal solution values. The values of Scc(0) for Bi-Cd alloy is close to the ideal Scc (0). The indication of the excess stability of Scc(0) for some alloys is in support of homocoordination. The Scc(0) and excess stability function of Scc (0) for the four alloys are presented.

Keywords: Concentration-concentration fluctuation, Excess stability function, Ordering energy.

Introduction

The neutron diffraction experiment in particular is a very useful tool to obtaining structural information and thermodynamic properties of binary liquid alloys [1]. In most cases, obtaining the experimental data needed for the calculation of specific thermodynamic properties is not a problem (except in some uncommon cases where the experimental data for some alloys may not be available due to cumbersome task involved and experimental difficulties). In principle, Short Range Order (SRO) which has a relationship with Concentration-Concentration Fluctuation in the long wave length limit (Scc (0)) in the literature can be experimentally determined from the knowledge of concentration-concentration partial structural factor, S_{cc} (q) and the number-number partial structural factor S_{NN}(q) [2]. However, these structures are not easily measurable in most diffraction experiments. Hence, SRO is usually computed without necessarily making reference to its experimental values. Additionally, a direct experimental determination of Scc (0) is often avoided due to complexities involved. For this reason, the option of thermodynamic model which is readily used was employed.

In this study, ordering energy values were determined from Scc (0) [3] of which four alloys were considered and in the application of the thermodynamic model using the determined values of ordering energy, the values of Scc(0) and ES were calculated at various temperatures [4].

The calculations of the thermodynamic quantities at different temperatures involve getting the available experimental data and employing a suitable theoretical model. These four candidates (Cd-Ga, Ag-Ge, Al-Au and Bi-Cd liquid alloys) under observation are those with variations in the values of thermodynamic quantities at various temperatures. To be specific, application is therefore made to these alloys which belong to a hereocoordinated and

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self-coordinated group of alloys. The alloys were preferred because all of them represent the classes of metals and semiconductors.

Investigations of liquid metallic alloys on the basis of Quasi Lattice Model (QLM) and its usage for extracting values are also found in [5-7], where this model was used for the calculation of some thermodynamic properties of compounds forming binary molten alloys at their melting temperatures.

In this observation, the QLM was applied to Cd-Ga, Ag-Ge,Al-Au and Bi-Cd liquid alloys for the qualitative investigation of their thermodynamic properties. Ordering energy values determined from Scc (0) are recorded in Table 1. Programs were inscribed to generate data for thermodynamic expressions as functions of concentration, c, using ordering energy values, w, coordination number, Z, Boltzmann constant, K and temperature, T presented in Table 1.

TABLE 1. Ordering energy (w) in eV of binary alloys

Alloy	Temperature (^oK)	Z	W_1(eV)
Cd-Ga	700	10.0	0.1133
Ag-Ge	1250	10.0	0.0288
Al-Au	1338	10.0	0.0980
Bi-Cd	773	10.0	0.0210

Theory

The calculation of Scc(0) needs on attachment like Excess Stability Function (ES). The variation of this quantity with composition is informative. This view provides facts that shed light on monotonous behavior of excess stability function of nearly ideal solutions with values approaching zero, although it will exhibit one or more peaks for solutions with strong chemical interactions. The positions of peaks correspond to compositions in which ordering (chemical short-range or intermediate-range) will occur. For an ideal solution Scc(0) = X_1X_2, whereas for an alloy exhibiting formation, Scc(0) exhibits one or more dips with values close to zero. Consequently, a maximum in ES corresponds to a minimum in Scc(0). The width and the height of the dip in Scc(0) and the peaks in Es can be shown to be related to the degree and extent of stability of the complex entities. Thermodynamically, the relationship between short-range order parameter: SRO, concentration-concentration fluctuation, Scc(0) and other thermodynamic properties had been sighted in the literature [8-10]. Moreover, between Es and Scc(0), it is given below. The following thermodynamic expressions are from Quasi Lattice Model.

Quasi Lattice Expressions for Various Thermodynamic Functions

Concentration-Concentration Fluctuation in the Long Wavelength Limit

$$Scc(0) = \frac{c(1-c)}{(1+(\frac{Z}{2\beta})(1-\beta)} \tag{1}$$

where $\eta = \exp(w/ZKT)$ (2)

and Z is the coordination number for the first shell, w is the ordering energy, K is the Boltzmann constant, T is the temperature, c is the concentration of atom A and 1-c is the concentration of atom B;

where $\beta = (1+4c(1-c)[(\eta)(\eta)-1])^{0.5}$ (3)

η and β are thermodynamic parameters which are interwoven.

Excess Stability Function (ES)

$$ES = \frac{RT}{Scc(0)} - \frac{RT}{c(1-c)} \tag{4}$$

Ideal Concentration - Concentration Fluctuation in the Long Wavelength Limit

$$Scc_{cc}^{id}(0) = c(1-c) \tag{5}$$

R is the molar gas constant.

Results

TABLE 2. Calculated experimental Scc(0) and ES of Cd-Ga alloy using experimental activity. C_{Cd} is the concentration of cadmium in the alloy at 700 ^OK.

C_{Cd}	Scc(0)	Scc(0)id	ES (10^{-3} J/mol)
0.0	0.0000	0.00	0
0.1	0.170	0.09	-30.4301
0.2	0.437	0.16	-23.0545
0.3	0.976	0.21	-21.7494
0.4	1.718	0.24	-20.8615
0.5	1.745	0.25	-20.0060
0.6	1.143	0.24	-19.1580
0.7	0.638	0.21	-18.5918
0.8	0.347	0.16	-19.6044
0.9	0.228	0.09	-39.1390
1.0	0.0000	0.00	0

TABLE 3. Calculated experimental Scc(0) and ES of Ag-Ge alloy using experimental activity. C_{Ag} is the concentration of silver in the alloy at 1250 ^{O}K.

C_{Ag}	Scc(0)	Scc(0)id	ES(10^{-3} J/mol)
0.0	0.0000	0.00	0
0.1	0.112	0.09	-22.6814
0.2	0.193	0.16	-11.1067
0.3	0.262	0.21	-9.8438
0.4	0.303	0.24	-9.084
0.5	0.288	0.25	-5.4856
0.6	0.222	0.24	3.5102
0.7	0.153	0.21	18.4363
0.8	0.104	0.16	37.9742
0.9	0.076	0.09	21.2714
1.0	0.0000	0.00	0

TABLE 4. Calculated experimental Scc(0) and ES of Al-Au alloy using experimental activity. C_{Al} is the concentration of Aluminum in the alloy at 1338 ^{O}K.

C_{Al}	Scc(0)	Scc(0)id	ES (10^{-3} J/mol)
0.0	0.0000	0.00	0
0.1	0.180	0.09	-61.7979
0.2	0.313	0.16	-33.9859
0.3	0.372	0.21	-23.0680
0.4	0.412	0.24	-19.3508
0.5	0.422	0.25	-17.4960
0.6	0.403	0.24	-18.6982
0.7	0.251	0.21	-8.6549
0.8	0.268	0.16	-28.0182
0.9	0.151	0.09	-49.9314
1.0	0.0000	0.00	0

TABLE 5. Calculated experimental Scc(0) and ES of Bi-Cd alloy using experimental activity. C_{Bi} is the concentration of bismuth in the alloy at 773 ^{O}K

C_{Bi}	Scc(0)	Scc(0)id	ES(10^{-3} J/mol)
0.0	0.0000	0.00	0
0.1	0.089	0.09	-0.8023
0.2	0.166	0.16	-1.4516
0.3	0.250	0.21	-4.8961
0.4	0.296	0.24	-4.6168
0.5	0.296	0.25	-3.5459
0.6	0.256	0.24	-1.6736
0.7	0.204	0.21	0.9004
0.8	0.156	0.16	1.0310
0.9	0.065	0.09	27.4645
1.0	0.0000	0.00	0

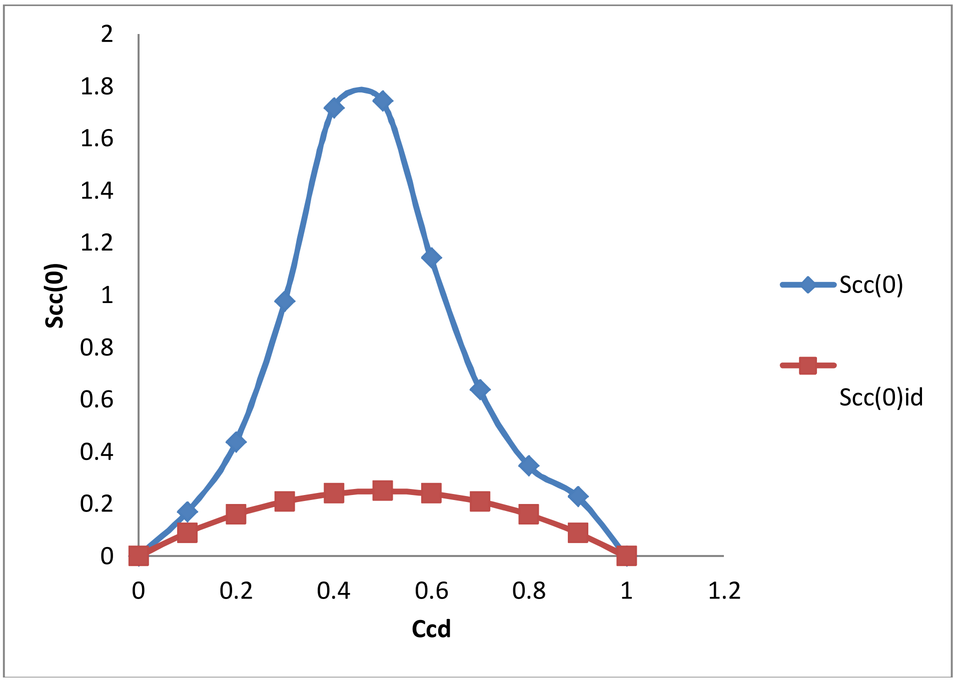

FIG. 1. Scc(0) of Cd-Ga against concentration C_{Cd}.

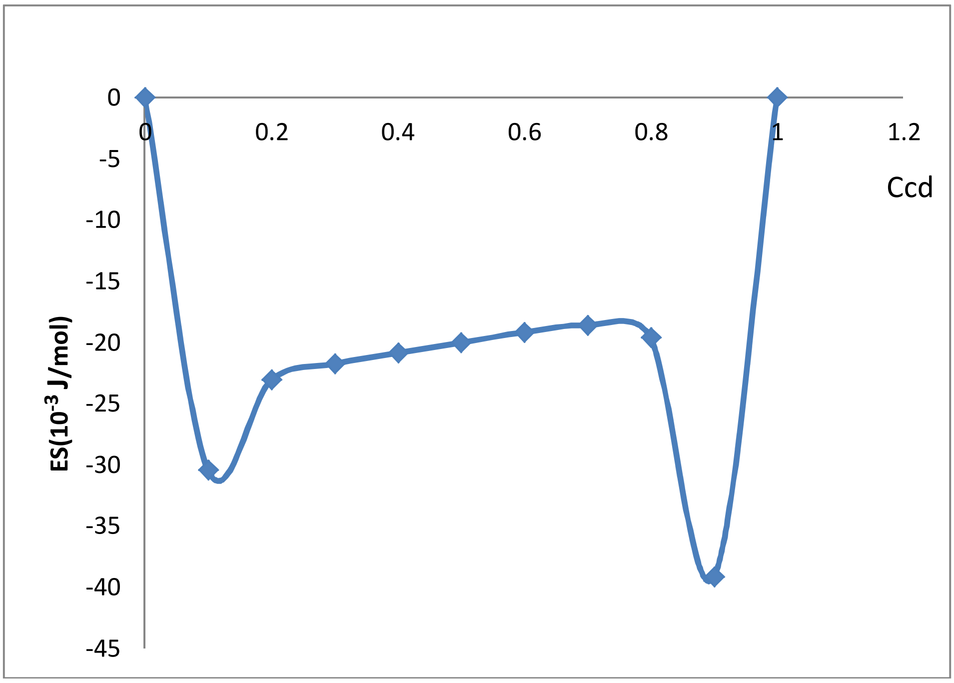

FIG. 2. ES of Cd-Ga against concentration C_{Cd}.

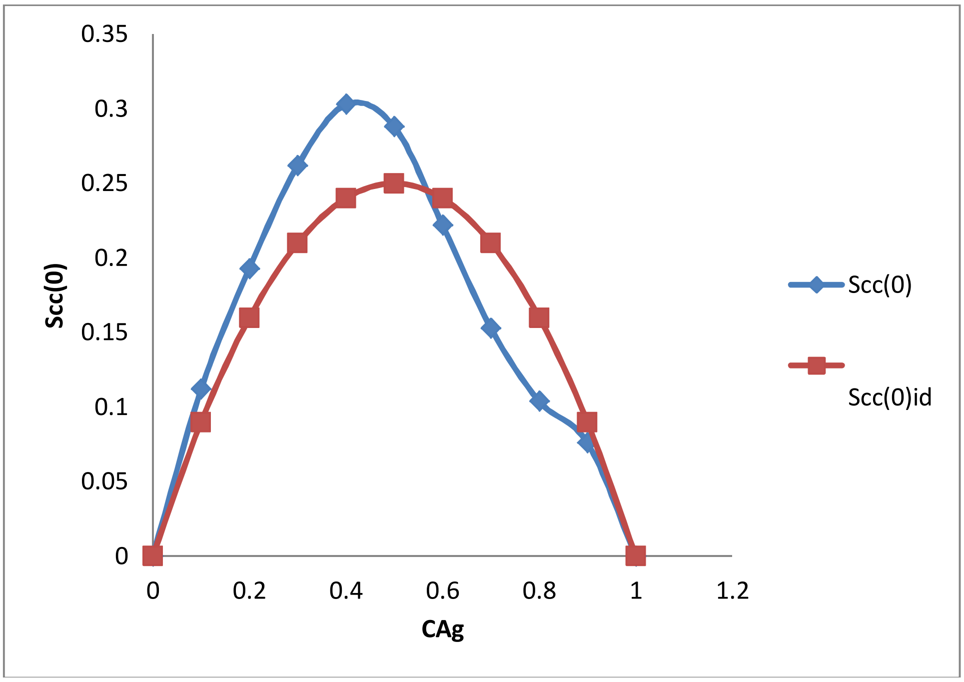

FIG. 3. Scc (0) of Ag-Ge against concentration C_{Ag}.

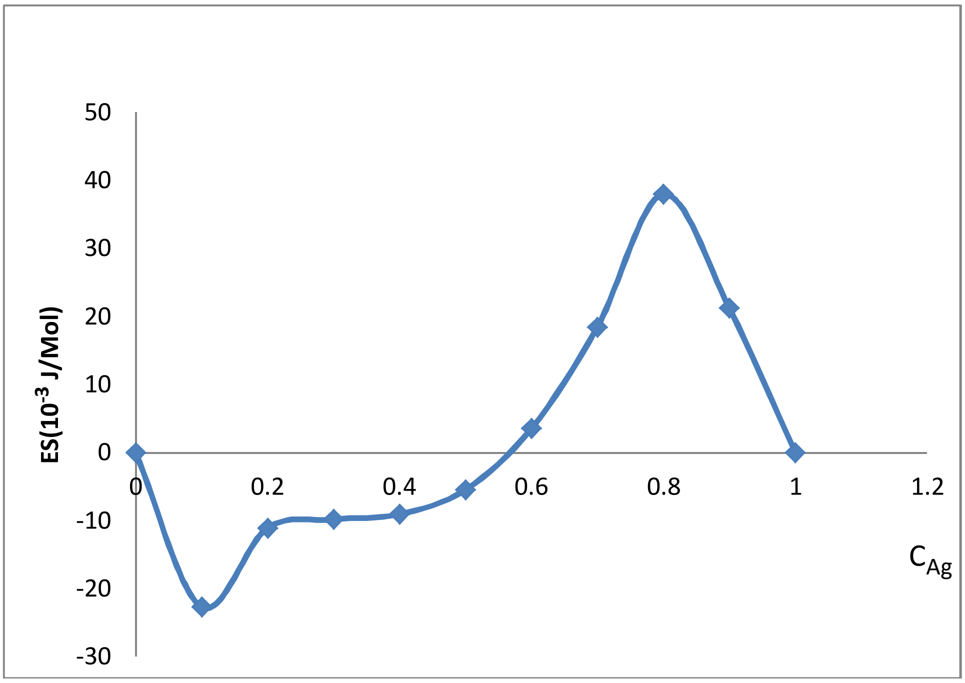

FIG. 4. ES of Ag-Ge against concentration C_{Ag}.

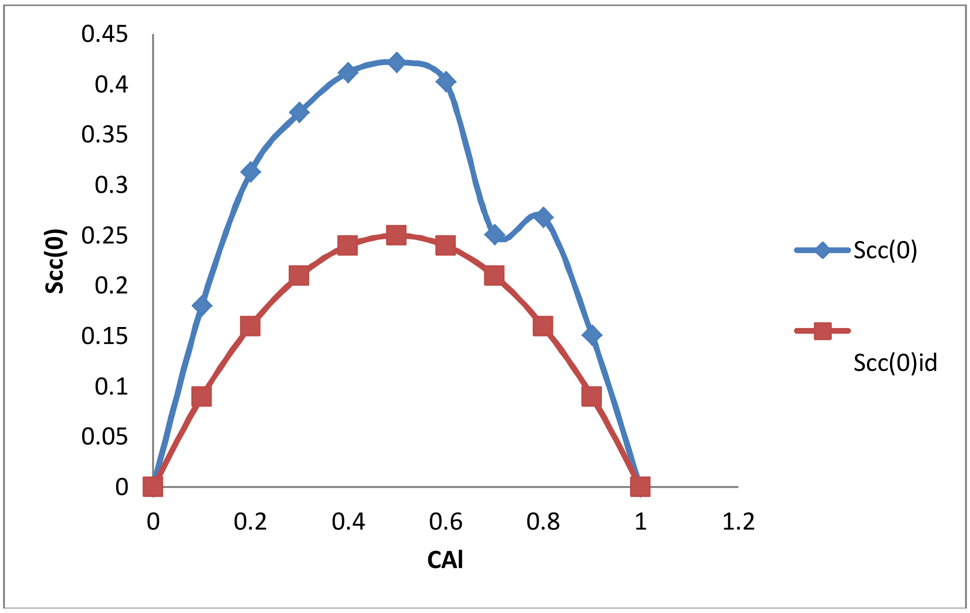

FIG. 5. Scc (0) of Al-Au alloy against concentration C_{Al}.

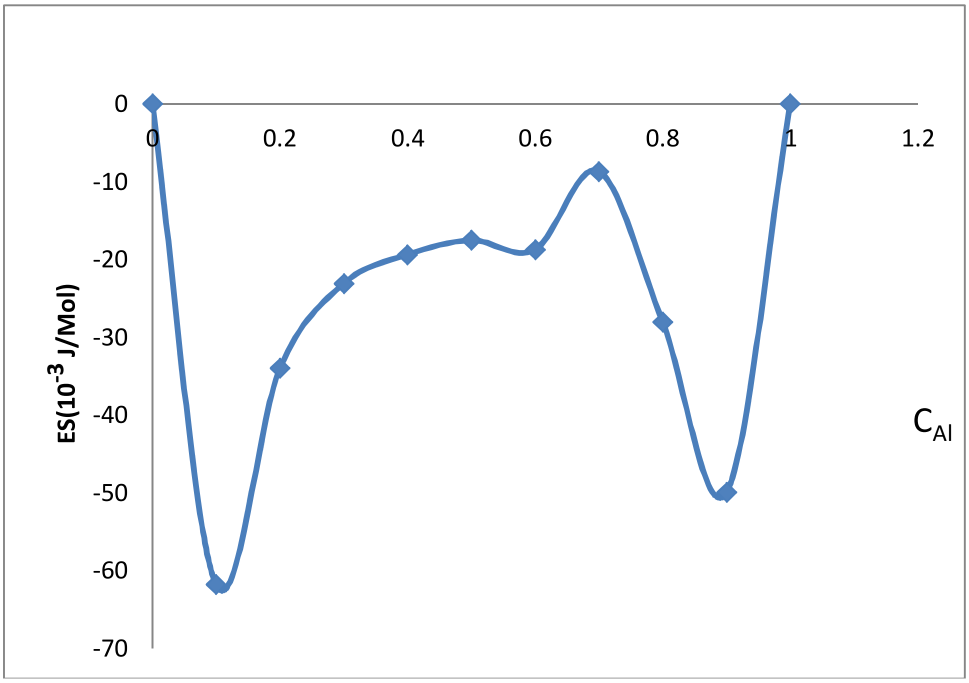

FIG. 6. ES of Al-Au alloy against concentration C_{Al}.

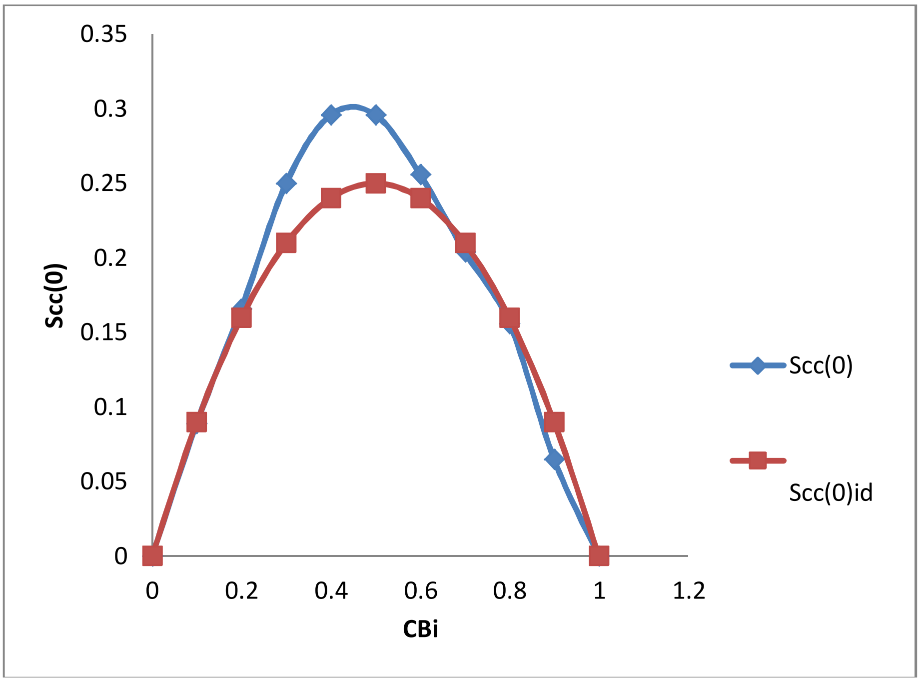

FIG. 7. Scc(0) of Bi-Cd against concentration C_{Bi}.

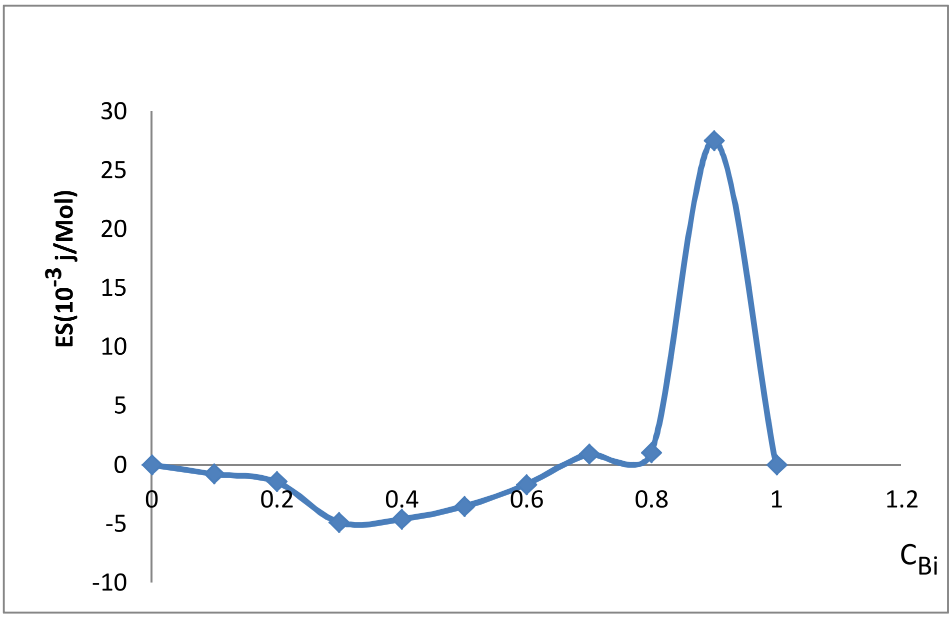

FIG. 8. ESof Bi-Cd against concentration C_{Bi}.

Discussion

Figs. 1, 3, 5 and 7 show the plots of concentration-concentration fluctuation Scc (0) against concentration of element for Cd-Ga, Ag-Ge, Al-Au and Bi-Cd liquid alloys at their melting temperatures. The Scc(0) of these alloys increases initially to a maximum (owing to the charge transfer between neighboring atoms) within the entire concentration range with distinct peaks at C_{Cd} = 0.5, C_{Ag} = 0.4 and C_{Bi} = 0.4 and the remaining liquid alloy has some depression at the right side of the curve (owing to chemical alternation of positive and negative charges with length scale approximately twice the nearest neighbor distance) at C_{Al} = 0.7. In Fig. 5, the curve of Scc (0) against C_{Al} of aluminum-gold alloy rises above the ideal solution curve (because of the topological short-range order; i.e., geometrical arrangements of atoms), indicating homocoordination (preference of like atoms as the nearest neighbors). Fig. 3 has an ideal solution curve intersecting with the curve of Scc (0) at concentration between C_{Ag} = 0.5 and 0.6 because of directional bonding. In Fig. 7, the calculated Scc (0) is in perfect agreement with ideal solution values at points C_{Bi} = 0, 0.1, 0.2, 0.7, 0.8 and 1.0, but with observed disagreement at points C_{Bi} = 0.3, 0.4, 0.5, 0.6 and 0.9. This is because there is a near cancellation of the ionic potentials, while at large distances ionic potentials were screened. Fig. 7 also has its calculated values for Scc(0) of Cd-Ga above the ideal solution values, which is in support of homocoordination or self-coordination.

Figs. 2, 4, 6 and 8 show the plots of excess stability function *versus* concentration of element. The display in Fig. 2 shows an initial decrease in the curve to a minimum (possibly when the disordered potential is too large) with a corresponding gradual increase and some fluctuations with concentration. The excess stability function has negative values; it falls downward to concentration C_{Cd} = 0.1 before ascending in a straight line between C_{Cd} = 0.2 and 0.8 eventually with a repetition of what was displayed at C_{Cd} = 0.1 being also displayed at C_{Cd} = 0.9 with minimum excess stability function between C_{Cd} = 0.8 and 1.0 which was lower than what was observed at the initial stage of the curve. The excess stability function displayed in Fig. 4 shows an initial decrease as the concentration increases and subsequent increase in concentration makes excess stability function reach the highest value. In Fig. 6, the display shows the short-range repulsive potential which prevented the atoms of Au and Al from reaching each other, thereby allowing the Es values to be completely negative throughout the concentration. In Fig. 8, as the concentration increases, there was a corresponding decrease in the excess stability function (due to interatomic potentials repelled by the central potential) between C_{Bi} = 0.2 and 0.6 with negative significance. A sharp increase in excess stability up to maximum value (due to pair correlation function thus formed at a distance a little greater than the effective diameter) in the concentration range C_{Bi} = 0.8-0.9 was observed before falling sharply to zero excess stability function at C_{Bi} = 1.0. Lastly, the peaks of excess stability function were obtained in the concentration range of 0.8 for Ag-Ge and 0.9 for Bi-Cd, except for Al-Au and Cd-Ga liquid alloys.

Conclusion

Ag-Ge and Bi-Cd liquid alloys are chemically strong interacting compounds with chemical short-range order. The dip in Al-Au liquid alloy is an indication of slight formation. The width and height of excess stability function at a specific concentration for Ag-Ge is a candidate of stability possibly in excess. The narrow width and considerable height of excess stability function for Bi-Cd are described with strong stability and Cd-Ga liquid alloy is a weak interacting system with an intermediate range.

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