Thermodynamic Properties, Surface Properties and Volume of Mixing of Liquid Cd-Na Alloys – Complex Formation Model Incorporating Volume Interaction Terms

A.K. Mishra

Department of Physics, Sabour College, Sabour - 813210, Bhagalpur, Bihar, India.

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ABSTRACT

A complex formation model incorporating volume interaction terms is considered to study thermodynamic properties, surface properties and volume of mixing of CdNa liquid alloys. Of the two intermediate phases Cd_2Na and $\text{Cd}_{11}\text{Na}_2$ in the solid state, Cd_2Na is assumed to exist in the liquid state due to its higher melting temperature. The evaluated values of interaction energies suggest that the system CdNa is dominated by repulsive forces. The model is successful in explaining the weak thermodynamic mixing properties and strong volume contraction of CdNa liquid alloy. The study of surface properties reveals that Na atoms segregate at all bulk concentrations being more up to 50% concentration of Cd.

Key words: Repulsive force, Complex formation, Interaction energy, Segregation, Phase separation, Size factor, Electronegativity, Chemical equilibrium.

1. INTRODUCTION

A thermodynamic investigation appears to be worthwhile since structural irregularities are always paralleled by specific deviation from the ideal thermodynamic behaviour. The heterocoordination i.e., preference for unlike atoms to pair as nearest neighbours and the homocoordination i.e., preference for like atoms to pair as nearest neighbours help to analyse the compound forming tendencies and the phase

separation in binary liquid alloys. The inter-atomic forces or contributions from entropy and enthalpy to the free energy /1–4/ have been identified as the physical reasons responsible for phase separation. The ideal associated solution model /5–7/ and the method by Jordan /8/ neglecting the interactions between the complex and the free atoms do not take into account the volume interactions associated with the formation of the complex. Bhatia and Hargrove /9/, Jacob *et al* /10/ and Srikanth and Jacob /11/ incorporated the volume effects in the solution model. In these methods the volumes of the free atoms are considered equal and that of complex is taken stoichiometrically related to the volume of free atoms. But size reduction is expected due to strong bonding.

Recently, volume interaction terms have been incorporated by Srikanth /12/ and Jha *et al* /13/ to calculate the volume of mixing of Mg–Sn and Hg–Na liquid alloys, respectively, along with the thermodynamic properties. Mg–Sn is a weak interacting system /7,14–16/ and its volume of mixing is not experimentally known. Hg–Na is a strong interacting system /17–19/ and there is much volume contraction of about 17.7% /20/. But the concentration properties of Cd–Na liquid alloys are interesting in many ways. Cd–Na liquid alloy is a weak interacting system ($G_M/RT < -3.0$) /21/ but much volume contraction of about 14.7% is observed /22/. The concentration fluctuations at the long wavelength limit ($S_{cc}(0)$) are greater than ideal concentration fluctuations ($S_{cc}(0) = C_1 C_2$; C_1 and C_2 are concentrations of first and second species respectively) in the concentration range

$C_1 < 0.53$ /23/. This shows that at some concentrations short-range order exists while segregation occurs at other concentrations. The phase diagram /21/ indicates a wavy liquidus line with a small hump around the stoichiometric composition Cd_2Na . Cd and Na have respectively; hcp and bcc crystal structures whereas on alloying Cd_2Na has a cubic structure. The size factor ($\Omega_{\text{Na}}/\Omega_{\text{Cd}}$, Ω is the atomic volume) of 1.77 and electro negativity difference ($\text{EN} = 1 - \exp(-0.25d^2)$, d is the difference in EN values of the two metals) of 0.1478 are small to account for anomalous behaviour. An understanding of surface segregation and surface tension is essential in the study of catalytic activity and metallurgical operations /24–28/. Moreover, liquid Cd alloys are highly reactive in nature /28,29/ due to which diffraction experiments are difficult to perform. These anomalous concentration properties of CdNa prompted calculation of the free energy of mixing, enthalpy of mixing, entropy of mixing, activity, volume of mixing and surface tension of CdNa liquid alloys.

A complex formation model /30–33/ incorporating volume interaction terms /12,13/ is considered for the study of thermodynamic and surface properties of CdNa liquid alloys. The alloy forms two intermediate phases namely γ (Cd_2Na) and β ($\text{Cd}_{11}\text{Na}_2$) in the solid state. The chemical complexes like Cd_2Na are assumed to exist in the liquid state since the γ -phase has a higher melting temperature. Thus the alloy consists of a mixture of Cd atoms, Na atoms and a number of chemical complexes like Cd_2Na , all in chemical equilibrium with one another.

The expressions have been obtained in Section 2 and Section 3 deals with the results. Some discussions are provided in Section 4.

2. COMPLEX FORMATION MODEL INCORPORATING VOLUME INTERACTION TERMS

2.1. Number of complexes and free energy of mixing

The number of complexes n_3 is obtained through the condition

$$(\partial G_M / \partial n_3)_{T,P,C} = 0 \quad (1)$$

The free energy of mixing (G_M) comprising of free

atoms n_1, n_2 and complex given by /12,13/

$$G_M = -n_3 g + RT \sum_{\substack{i,j=1 \\ i < j}}^3 (n_j \ln(\phi_j) + n_i \phi_j W_{ij}) \quad (2)$$

$$\begin{aligned} \text{Here, } n_1 &= C_1 - \mu n_3 \\ n_2 &= C_2 - \nu n_3 \\ n &= n_1 + n_2 + n_3 \end{aligned} \quad (3)$$

μ and ν are small integers and C_1, C_2 are, respectively, the concentrations of first and second species of the alloy.

W_{ij} in Eq. (2) are the interaction energies and the first term ($-n_3 g$) lowers the free energy of the alloy due to the formation of chemical complexes. The energy of formation (g) of the complex is given by

$$g = -RT \ln K \quad (4)$$

R is the gas constant, T is the specified absolute temperature and K is the equilibrium constant for the dissociation reaction $A_\mu B_\nu \rightleftharpoons \mu A + \nu B$. If V_1, V_2, V_3 be the volumes of free atoms A, B and complex $A_\mu B_\nu$ respectively then

$$\phi_j = n_j V_j / V \quad (5)$$

V is the volume of the alloy.

The equilibrium constant K can be expressed in terms of model parameters as

$$K = K_1 \cdot \exp(\mu + \nu - 1) \quad (6)$$

with

$$K_1 = \exp(-Z) \cdot (\phi_1 \phi_2) / (\phi_3 V_D) \quad (7)$$

$$\begin{aligned} Z &= (\delta n_1 \phi_2 - \nu n_1 V_2 - \mu n_2 V_2) W_{12} + \\ &(\delta n_1 \phi_3 + n_1 V_3 - \mu n_3 V_3) W_{13} + \\ &(\delta n_2 \phi_3 + n_2 V_3 - \nu n_3 V_3) W_{23} / VRT \end{aligned} \quad (8)$$

$$V_D = \exp(\delta n / V) \quad (9)$$

δ is the volume shrinkage due to formation of the complex given by

$$\delta = \mu V_1 + \nu V_2 - V_3 \quad (10)$$

Equations (4) and (6) yield

$$(\phi_1, \phi_2) / (\phi_3 V_D) = \exp(-g/RT) \cdot \exp(Z) \cdot \exp(1-\mu-\nu) \quad (11)$$

2.2. Enthalpy and entropy of mixing

The enthalpy of mixing H_M can be obtained through Eq. (2) and relation

$$H_M = G_M - T(\partial G_M / \partial T)_{P,C,N} \quad (12)$$

$$\text{i.e., } H_M = -n_3 (g - T(\partial g / \partial T)) + \sum \sum n_i \phi_j (W_{ij} - T(\partial W_{ij} / \partial T)) \quad (13)$$

The entropy of mixing is given by

$$S_M = (H_M - G_M) / T \quad (14)$$

2.3. Volume of mixing

The volume change associated with the mixing of free atoms to form a liquid binary alloy may be expressed as

$$\Delta V = V - (C_1 V_1 + C_2 V_2) \quad (15)$$

V is the molar volume of the liquid alloy given by

$$V = n_1 V_1 + n_2 V_2 + n_3 V_3 \quad (16)$$

Volume interaction terms V_{ij} are to be introduced in Eq. (16) if volume of mixing is significantly influenced by the interactions among the different components in the binary liquid alloys. V is now given by

$$V = n_1 V_1 + n_2 V_2 + n_3 V_3 + \sum \sum n_i n_j V_{ij} \quad (17)$$

2.4. Activity

The activities of the unassociated component species may be expressed as

$$RT \ln a_i = (\partial G_M / \partial n_i)_{T,P,N} \quad (i = 1, 2) \quad (18)$$

From Eqs. (2) and (3) one gets ($W_{ir} = 0 = V_{ir}$ for $i = r$)

$$\ln a_i = (1 + \ln \phi_i - n V_i / V) - (n/V) \sum (n_r V_{ir}) + (n_i / n_i \phi_2 W_{12} + \phi_3 W_{13}) - (1/V) \sum (n_r \phi_s W_{rs}) (V_i + n_r V_{ir}) / (RT) \quad (19)$$

$r < s$

The terms with V_{ir} arise due to volume interaction terms.

Now,

$$\ln a_1 = (1 + \ln \phi_1 - n V_1 / V) - (n/V) (n_2 V_{12} + n_3 V_{13}) + (\phi_2 W_{12} + \phi_3 W_{13}) - (1/V) (n_1 \phi_2 W_{12} + n_1 \phi_3 W_{13} + n_2 \phi_3 W_{23}) (V_1 + n_2 V_{12} + n_3 V_{13}) / (RT) \quad (20)$$

$$\ln a_2 = (1 + \ln \phi_2 - n V_2 / V) - (n/V) (n_1 V_{12} + n_3 V_{23}) + (n_1 / n_2 \phi_2 W_{12} + \phi_3 W_{23}) - (1/V) (n_1 \phi_2 W_{12} + n_1 \phi_3 W_{13} + n_2 \phi_3 W_{23}) (V_2 + n_1 V_{12} + n_3 V_{23}) / (RT) \quad (21)$$

2.5. Surface Tension

The surface tension of complex forming liquid alloys is given by [34,35]

$$\sigma = \sigma_1 + (RT/A) \ln (C_1^S / C_1) + (RT/A) \ln (\gamma_1^S / \gamma_1) \quad (22a)$$

$$= \sigma_2 + (RT/A) \ln (C_2^S / C_2) + (RT/A) \ln (\gamma_2^S / \gamma_2) \quad (22b)$$

Where σ_i ($i = 1, 2$) are the surface tensions of the pure components and A the mean atomic surface area. C_i^S and γ_i^S refer, respectively, to the concentration and activity coefficient of the i th component at the surface. γ_i^S is related to γ_i :

$$\ln \gamma_i^S = n (\ln \gamma_i \text{ containing } C_i^S) + q \ln \gamma_i \quad (23)$$

$$\gamma = a_i / C_i$$

where n and q , termed surface coordination fractions, are the fractions of the total numbers of nearest neighbours of an atom within the layer in which it lies and that in the adjoining layer, respectively, so that $n + 2q = 1$.

3. COMPARISON BETWEEN CALCULATION AND EXPERIMENT

3.1. Number of complexes and free energy of mixing

The free energy of mixing (G_M) of liquid CdNa alloys at 673K was taken from the compilation of Hultgren *et al* [21]. Eq.(11) has been used to compute the equilibrium values of number of complexes (n_3) and hence G_M via Eq.(2). The values of interaction energies (g, W_{ij}) computed for CdNa are

$$\begin{aligned} g/RT &= 0.8 & W_{12}/RT &= 1.5W_{13}/ \\ RT &= -0.5 & W_{23}/RT &= -0.04 \end{aligned}$$

The values of interaction energy thus evaluated suggest that Cd and Na atoms are repulsive whereas both the constituent atoms Cd and Na are attractive in nature with complex Cd_2Na .

The volume of free constituent atoms Cd and Na at specified temperature has been computed from experimental density data of Smithell's Metals Reference Book /36/. The computed values of n_3 and G_M versus concentration are shown for CdNa liquid alloy in the upper and lower parts of Fig.1, respectively. The experimental values of G_M /21/ are also shown in Fig.1. The peak exhibited by n_3 (Fig.1) around $C_2 = 0.3$ is the indication of complex formation at this concentration. Theoretical and experimental values of G_M are in good agreement. The asymmetric behaviour is noticed around compound forming concentration.

Fig. 1: Free energy of mixing (G_M/RT) and number of complexes (n_3) versus concentration (C_2) of liquid CdNa alloy.

3.2. Enthalpy and entropy of mixing

The enthalpy of mixing H_M and entropy of mixing are evaluated through Eq. (13) and (14) respectively. The values of H_M are found to be in poor agreement with experiment if energy parameters are taken as being temperature independent. Therefore, the energy

parameters are considered to vary with temperature to ascertain the variation of enthalpy and entropy of mixing with experimental values /21/. The temperature dependent energies are

$$\begin{aligned} \partial g/\partial T &= -1.95R & \partial W_{12}/\partial T &= 4.80R \\ \partial W_{13}/\partial T &= 1.20R & \partial W_{23}/\partial T &= -2.70R \end{aligned}$$

The values of enthalpy of mixing and entropy of mixing thus evaluated are shown in Fig. 2 along with experimental values /21/. It is seen from Fig. 2 that the computed values are in reasonable agreement with the experiment. The enthalpy of mixing is maximum around the complex forming concentration. The negative and positive values of entropy of mixing have also been reproduced.

Fig. 2: Heat of mixing (H_M/RT) and entropy of mixing (S_M/R) versus concentration (C_2) of liquid CdNa alloy.

3.3. Volume of mixing

The volume of mixing of CdNa liquid alloy is computed through Eq. /15/ using Eqs. (16) and (17) separately. The volume of complex Cd_2Na has been taken as 435.605 a.u. The computed values of $\Delta V/V$ have been depicted in Fig.3 together with the experimental observations /22/. From Fig. 3 it is revealed that the computed values of volume of mixing are in close agreement with the experiment when volume interaction terms are considered. The volume

interaction terms computed for CdNa liquid alloys are (in a.u.)

$$V_{12} = 95 \quad V_{13} = 100 \quad V_{23} = -140$$

Fig. 3: Volume of mixing ($\Delta V/V\%$) versus concentration (C_2) of liquid CdNa alloy.

3.4. Activity

The activities of Cd and Na ($\ln a_{Cd}$, $\ln a_{Na}$) in CdNa liquid alloy is calculated via Eqs. (20) and (21). These have been given in Table 1 along with the experimental values /21/. The evaluated activity ratio ($\ln(a_1/a_2)$) along with experimental observations /21/ has been shown in Fig. 4. Table 1 and Fig. 4 show the resemblance of evaluated and experimental values of $\ln$ of activities of Cd and Na in case of CdNa liquid alloys.

Fig. 4: Ratio of activity ($\ln(a_1/a_2)$) versus concentration (C_1) of liquid CdNa alloy.

Table 1
Activities of Cd ($\ln a_{Cd}$) and Na ($\ln a_{Na}$) in liquid CdNa alloy at 673 K.

C_2	$\ln a_{Cd}$		$\ln a_{Na}$	
	Present	Exp. /21/	Present	Exp. /21/
0.1	-0.240	-0.165	-3.862	-3.816
0.2	-0.598	-0.473	-1.809	-2.040
0.3	-0.887	-0.777	-0.970	-1.108
0.4	-1.081	-1.041	-0.631	-0.605
0.5	-1.263	-1.237	-0.440	-0.401
0.6	-1.456	-1.374	-0.307	-0.237
0.7	-1.686	-1.487	-0.205	-0.188
0.8	-1.983	-1.645	-0.127	-0.135
0.9	-2.444	-1.980	-0.065	-0.084

3.5. Surface Tension

Eq. (22a,b) was solved numerically to compute the surface tension, σ , of liquid CdNa alloys at $T = 673K$. n and q were treated as parameters and were taken to be equal to 0.5 and 0.25 respectively. The energy parameters required for the computation were the same as used for the bulk parameters. The mean atomic surface area, A , was calculated from the relation given by Laty *et al.* /37/ as

$$A = 1.12(V)^{1/3}$$

V is the volume of the alloy. We used the volume calculated through Eq. (17). The surface tensions of the constituent elements of the alloy at the specified temperature were taken from Smithell's Metals Reference Book /36/.

The computed values of σ and C_2^s versus bulk concentration for liquid CdNa alloys are depicted in Figs. 5. and 6 respectively. We could not compare our theoretical values with experimental values for want of experimental data. From Fig. 5 it is evident that Na atoms lower the surface tension of CdNa. The decrease in the surface tension is more up to the equiatomic concentration. The surface tension remains less than the ideal values ($\sum C_i \sigma_i$) at all the concentrations. From Fig. 6 it is evident that Na atoms are found to segregate to the surface at all the bulk concentrations. The

Fig. 5: Surfaces tension (σ) versus concentration (C_2) of liquid CdNa alloy.

Fig. 6: Surface concentration (C_2^s) versus bulk concentration (C_2) of liquid CdNa alloy.

segregation is more up to $C_1 < 0.53$. The prediction of segregation by the surface concentration is the same as was observed experimentally by Harda *et al* /23/ in the measurement of EMF and hence concentration fluctuations at the long wavelength limit in liquid NaCd alloy over a wide range of concentrations.

4. DISCUSSION

The complex formation model is found successful in the theoretical investigation of the concentration dependent mixing properties of CdNa liquid alloy when the volume of the alloy is also taken into consideration. The values of interaction energies thus evaluated suggest that the system CdNa is dominated by repulsive interaction. The negative values of G_M and H_M and negative as well as positive values of S_M have been reproduced indicating the presence of intermediate complex Cd_2Na . The interaction energies have been taken concentration independent because incorporation of concentration dependence of order potential /38/ is mere parametrization. However, these interaction energy parameters are temperature dependent.

The considered model explains not only the weak thermodynamic mixing properties ($G_{M\min} = -0.87 RT$, $H_{M\min} = -0.892 RT$) but also strong volume concentration (-15%) in liquid CdNa alloy. The volume interaction terms considered in the computation of volume of mixing show that the influence between constituent Cd and Na atoms is minimum. The interactions between Cd and Na atoms as well as between the Cd atoms and Cd_2Na complex increase the volume of the alloy whereas those between Na atoms and complexes Cd_2Na reduce the volume of the alloy.

The computed values of number of complexes (n_3), free energy of mixing (G_M/RT) and volume of mixing ($\Delta V/V\%$) with and without considering the volume interaction terms are given in Table 2. From Table 2 it is revealed that volume interaction terms bring an appreciable change of an average of 18.752% (maximum being 39.484%) in the volume of mixing. But there is only an average change of 0.720 % (maximum being 1.508 %) in n_3 and 2.386 % (maximum being 5.863%) in G_M . Although the ratio of the volume of free Cd and Na atoms is 1.77, the contrast behaviour, the tendency of compound formation being weak and strong

Table 2

Free energy of mixing (G_M/RT), number of complexes (n_3) and volume of mixing ($\Delta V/V\%$) of liquid CdNa alloy at 673 K (a) without volume interaction term and (b) with volume interaction terms

C_2	$-G_M/RT$		n_3		$-\Delta V/V\%$		Exp. /22/
	(a)	(b)	(a)	(b)	(a)	(b)	
0.1	0.5389	0.5705	0.0976	0.0971	10.361	6.270	7.837
0.2	0.7673	0.7982	0.1724	0.1698	16.916	12.166	12.388
0.3	0.8294	0.8528	0.1951	0.1924	17.786	14.381	14.687
0.4	0.8218	0.8336	0.1889	0.1877	16.085	14.517	14.735
0.5	0.7765	0.7763	0.1694	0.1695	13.532	13.564	13.566
0.6	0.7009	0.6918	0.1416	0.1422	10.652	11.707	11.794
0.7	0.5954	0.5826	0.1082	0.1090	7.691	9.116	9.285
0.8	0.4572	0.4463	0.0714	0.0719	4.814	5.968	6.896
0.9	0.2773	0.2732	0.0331	0.0333	2.124	2.542	3.863

contraction in volume is reproduced by complex formation model. The same interaction parameters were used to calculate the surface tension and surface concentrations of CdNa alloys. The study reveals that Na atoms segregate at the bulk concentration and the segregation is more upto $C_1 = 0.5$. Segregation is caused where the system is dominated by repulsive forces. In a binary mixture segregation is an outcome of the enthalpic contribution and only the mismatch size ratio is insufficient in doing so [4]. It is clear from above discussion that one may get observed volume of mixing, thermodynamic properties and surface properties of complex forming liquid alloys by the proper adjustment of interaction parameters, i.e., interaction energies along with volume interaction terms.

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