Interionic Pair Potential, hard sphere diameter and entropy of mixing of NaCd compound forming binary molten alloys under the framework of Pseudopotential theory

Sujeet Kumar Chatterjee [a], Lokesh Chandra Prasad[b], Ajaya Bhattarai [a, *]

[a] Department of Chemistry, Mahendra Morang Adrash Multiple Campus, Biratnagar, Tribhuvan University, Nepal

[b]P G Department of Chemistry, T M Bhagalpur University, Bhagalpur 812 007, India

bkajaya@yahoo.com (Ajaya Bhattarai)

ABSTRACT

The observed asymmetric behaviour of mixing of NaCd liquid alloys around equiatomic composition with smaller negative values for free energy of mixing at compound forming concentration, i.e. G_M^{XS} = -4.9KJ at C_{cd} =0.66, has aroused our interest to undertake a theoretical investigation of this system.

A simple statistical mechanical theory based on compound formation model has been used to investigate the energetics of formation of intermetallic compound Cd_2Na in the melt through the study of entropy of mixing.

Besides, the interionic interactions between component atoms Na and Cd of the alloys have been understood through the study of interionic pair potential $\phi_{ij}(r)$, calculated from pseudopotential theory in the light of CF model.

Our study of $\phi_{ij}(r)$ suggest that the effective interaction between Na-Na atoms decreases on alloying with Cd atom, being minimum for compound forming alloy($Cd_{0.66}$ $Na_{0.34}$).The nearest neighbor distance between Na-Na atoms does not alter on alloying. Like wise Na-Na, effective interaction between Cd-Cd atom decreases from pure state to NaCd alloys, being smaller at compound forming concentration $Cd_{0.66}$ $Na_{0.34}$.The computed values of S_M from pseudopotential theory are positive at all concentrations, but the agreement between theory and experiment is not satisfactory. This might be happening due to parameterisation of σ_3 and Ψcompound.

Indexing terms/Keywords

Interionic pair potential $\phi_{ij}(r)$,Entropy of mixing(S_M); Pseudopotential theory; Equiatomic composition; Intermetallic compound and binary molten alloys

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INTRODUCTION

The energetic of strong interacting binary liquid alloys were studied by using various theoretical models[1-6], based on the formation intermetallic compounds, pseudomolecules, complexes in the melt. Stronger interaction [7] corresponds to greater possibility of compound formation. The first principal theory in the frame-work of pseudopotential formalism can be used to calculate the pair-potential, which subsequently, can be used to study the interionic interaction [8-10], but pseudopotential theory, itself suffers from limitations. For those alloys, whose mixing properties exhibit anomalous behavior due to strong interaction between the unlike atoms, forming compounds, this theory cannot be applied with confidence [7,8,11]. In view of limitation, the pseudopotential theory requires improvement. An attempt has been made through this work to calculate interionic pair potential by incorporating the phenomena of compound formation in pseudopotential theory [12].

The hard sphere diameter has been evaluated by minimizing the pair-potential [8,13,14]. The computed hard sphere diameter has been utilized to evaluate the entropy of mixing of these alloys as a function of concentration. The concentration dependent thermodynamic properties [3, 14-17] are greatly affected by the formation of intermetallic compound in the melt. Without understanding the cause of anomaly, one cannot get the real picture of mixing behaviour of such alloys. With this view, we have used the CF model to investigate the concentration dependent entropy of mixing of NaCd binary liquid alloys.

Section (2) contains the theoretical formalism to hard sphere diameter, interionic pair-potential and entropy of mixing where as section (3) contains result and discussion and section (4) contains summary and Conclusion.

1. Theoretical formalism

1.1. Formalism

A binary liquid alloy containing in all N_A (= N (1-C) of atom A and N_B (= (NC) of atom B may be assumed to consist of $n_A(=n_1N)$ free atom of A, $n_B(=n_2N)$ free atom of B and $n_m(=n_3N)$ complexes which also act as independent scattering centers to the alloys.

The total numbers of scattering points are:

$$N_S = n_A + n_B + n_m = nN \quad (1)$$

Where

$$n = n_1 + n_2 + n_3 \quad (2)$$

From the Principle of conservation of atom, we have

$$n_A + \mu n_m = N_A \quad (3a)$$

$$n_B + \nu n_m = N_B \quad (3b)$$

$$n_1 = 1 - C - \mu n_3$$

$$n_2 = C - \nu n_3$$

$$n = 1 - (\mu + \nu - 1) n_3$$

Here ‘C’ is concentration of second species.

Volume in which N_A atoms of A and N_B atoms of B are randomly distributed can be expressed as

$$\Omega = \Omega_{alloy} - n_m V_m \quad (4)$$

where Ω_{alloy} is the atomic volume of the alloy and V_m is the volume of the complex .

$$V_m = \mu\Omega_1 + \nu\Omega_2 \quad (5)$$

where Ω_1 and Ω_2 are the atomic volumes of first and second species separately. We may recall that the hared sphere diameters σ_1 and σ_2 occurs as important ingredients, the value of σ_i(i=1,2) as a function of concentration, have been determined by minimizing the interionic pair potential φ i.e.

$$\varphi(\sigma_i) = \frac{3}{2} K_B T + \varphi_{\min} \tag{6}$$

where $\frac{3}{2} K_B T$ = mean Kinetic energy

$\varphi_{\min}$ = Depth of the first minimum in the interionic pair potential. Harrison[18] showed that the pairwise potential between the metallic ions can be evaluated from the band structure energy. By generalizing this formalism, one can obtain φ_{ij}(i,j=constituent elements) for binary alloys.

$$\varphi_{ij} = \frac{Z_i Z_j}{R}\left[1 - \frac{2}{\pi}\int_0^\infty F_{ij}^N \frac{Sinqr}{q} dq\right] \tag{7}$$

where Z_i, Z_j= Valencies of the constituent elements.

F_{ij}^N = Normalised wave number characteristics i.e.

$$F_{ij}^N = -\left(\frac{q^2\Omega}{2\pi Z_i Z_j}\right) F_{ij}(q) \tag{8}$$

Where $F_{ij}(q)$ are partial energy wave number characteristics. $F_{ij}(q)$ in the local approximation can be expressed as

$$F_{ij}(q) = -\frac{\Omega q^2}{8\pi}\left[W_i^0(q) W_j^0(q) . \frac{\varepsilon^*(q) - 1}{\varepsilon^*(q)} . \frac{1}{1 - G(q)}\right] \tag{9}$$

where $W_i^0(q)$ and $W_j^0(q)$ are the unscreened form factors of i and j components respectively.

The interionic pair potential for Na-Cd liquoid alloys are obtained through eq. (7) at different concentration, the unscreened form factor $W_0(q)$ of the constituent species are obtained using Heine-Abarenkov(HA)model potential [19] as

$$W^0(q) = -\left(\frac{4\pi Z}{\Omega q^2}\right) Cosqr_m - \left(\frac{4\pi A}{\Omega q^3}\right)(Sinqr_m - qr_m Cosqr_m) \tag{10}$$

$\varepsilon^*(q)$= Modified Hartree dielectric function, expressed as

$$\varepsilon^*(q) = 1 - (\varepsilon(q) - 1)(1 - G(q)) \tag{11}$$

where $\varepsilon(q)$ is the usual Hartree dielectric constant.

G(q) takes into account of the exchange and correlation effect of the conduction electrons. In our work, we have taken [20] expression for G(q) as

$$G(q) = A\left[1 - \{\exp(-B(\frac{q}{K_F})^2\}\right] \tag{12}$$

K_F = Fermi wave vector for compound forming alloys, may be expressed as

$$K_F^3 = \frac{3\pi^2[1 - C)Z_i + (Z_i - Zn_m)/N]n}{\Omega_{alloy} - n_m V_m} \tag{13}$$

A and B in eq.(12) are constants, given by r_s (Wigner- Seitz) radius, which is expressed as

$$r_s = \left[\frac{3(N\Omega - n_m V_m)}{4\pi\eta}\right]^{1/3} \tag{14}$$

The packing density η for compound forming alloys,

$$\eta_p = \frac{\pi}{6\Omega_{alloy}} \sum_{i=1}^{3} X_i Z_i^3 \tag{15}$$

X_i= concentration fraction of scattering centres. The hard sphere diameter for compound forming system is determined via eqs. (6) and (7) using the value of K_F, r_s and η given by eqs. (13), (14) and (15) respectively.

1.2 . Entropy of mixing for compound forming system

The complex formation model allow us to express entropy of mixing of complex forming liquid alloys [11], (5) as

$$S_M = S_{gas} + S_c + S_\eta + S_\sigma + S_{comp.} \tag{16}$$

where the contribution of the Pseudomolecules A_μ and B_v has been accounted.The gas term S_{gas} is given by

$$\frac{S_{gas}}{K_B} = \eta\left[2.5 + \ln\{\Omega_s (\frac{m_1^{x_1} m_2^{x_2} m_3^{x_3} K_B T}{2\pi h^2})^{3/2}\}\right] \tag{17}$$

where m_1,m_2, m_3 are the masses of constituent atoms and complex respectively. $\Omega_s = (\Omega/N)$ is the scattering volume of the alloy in which free electrons travel, K_B is the Boltzman constant and T is the required temperature. S_c is the ideal mixing term.

$$\frac{S_{gas}}{K_B} = -n(X_1 \ln X_1 + X_2 \ln X_2 + X_3 \ln X_3) \tag{18}$$

The total packing term S_η is given by

$$\frac{S_\eta}{K_B} = -n(r-1)(r+3) \tag{19}$$

with r=1/1-η

η is the packing density given by

$$\eta = \frac{\pi}{\Omega_{alloy}} \sum X_i \sigma_i^3 (i = 1,2,3) \tag{20}$$

where σ_1 and σ_2 are the densities of the constituent atoms 1 and 2 and σ_3 is the diameter of the complex S_σ arises due to the difference among the diameters of the free atoms and complex is given by

$$\frac{S_\sigma}{K_B} = S_\sigma(1,2) + S_\sigma(1,3) + S_\sigma(2,3) \tag{21}$$

where $$S_\sigma(i,j) = X_i X_j (\sigma_i - \sigma_j)^2 \left\{[r(r-1) - \ln r](\beta_1^{ij} + \beta_2^{ij}) + 3(r-1)\beta_1^{ij}\right\} \tag{22}$$

where (i,j=1,2,3)

$$\beta_1^{ij} = \frac{\sigma_i + \sigma_j}{\sigma^3} \tag{23a}$$

$$\beta_2^{ij} = \sigma_i \sigma_j (X_1 \sigma_1^3 + X_2 \sigma_2^3 + X_3 \sigma_3^3) \tag{23b}$$

$$\sigma^3 = (X_1\sigma_1^3 + X_2\sigma_2^3 + X_3\sigma_3^3) \tag{23c}$$

S_{comp} is the contribution from the internal degree of freedom of the complexes, which is due to internal modes of vibration. It is approximated by a sum of contributions from each complex Ψ_{comp} may be written as

$$\frac{S_{comp}}{K_B} = n_3\Psi_{comp} \tag{24}$$

According to eq. (16), the entropy of mixing of complex forming liquid alloys can be expressed as,

$$S_m = \Delta S_{gas} + \Delta S_\eta + S_c + S_\sigma + S_{comp.} \tag{25}$$

where

$$\Delta S_i = S_{i,alloy} - C_A S_{i1} - C_B S_{i2} \tag{26}$$

(i=gas, η)

S_1 and S_2 are entropies of pure components whose explicit expression can be obtained by setting either C=0 or C=1.

RESULTS AND DICUSSSION

1.3. *Interionic pair-potential $\phi_{ij}(r)$*

The interionic pair-potential $\phi_{ij}(r)$, of NaCd liquid alloys have been computed using eq. (7).The wave number characteristics F_{ij}^N and Fermi wave vector K_F are obtained from eqs. (9) and (13) respectively. The model parameters used for these computations are taken from the work of Ese & Reissland[21], which is tabulated in the Table 1.

Table 1. Model parameters for HA form of Potential.

System	Na	Cd
A_o	0.312	0.936
R_o	3.209	2.136

The volume of mixing of Na-Cd liquid alloys was obtained from the work of Hoshino and Endo[22] which is given in Table 2.

Table 2. Volume diameter and ratio of diameter (α) for CdNa liquid alloys at 673K

C_{Cd}	Volume	σ_{Cd}	σ_{Na}	$\alpha = \sigma_{Cd}/\sigma_{Na}$
0.0	300.616	--------------	6.130	----------------
0.1	274.817	5.085	6.145	0.83
0.2	252.384	5.103	6.175	0.83
0.3	232.192	5.124	6.164	0.83
0.4	214.245	5.147	6.167	0.83
0.5	197.420	5.168	6.166	0.84
0.6	182.838	5.186	6.162	0.84
0.7	170.499	5.200	6.155	0.84
0.8	162.650	5.210	6.149	0.84
0.9	158.160	5.216	6.143	0.84
1.0	158.160	5.219	----------------	----------------

Heine-Abarenkov(HA)model potential has been used to determine the form factor $W^0(q)$ through eq. (10). A and B required for the calculation of G(q) from eq. (12) are fixed from Wigner-Seitz radius, r_s , which has been obtained from eq.

(14). The computed values of $\phi_{ij}(r)$, for Na-Cd system at different concentrations, have been presented in the figs. 1-3, for perusal and have been discussed with reference to pure state.

The computed values of pair potential between Cd-Cd atoms ($\Phi_{cd\text{-}cd}$) and Na-Na atoms ($\Phi_{Na\text{-}Na}$) in NaCd alloys, ($Cd_{0.5}$ $Na_{0.5}$ and $Cd_{0.66}$ $Na_{0.34}$) as a function of r are plotted in figures. 1-3. The effective interaction fig. (1) between Na-Na atoms decrease on alloying wih Cd atoms, being maximum at compound forming concentration. The nearest neighbour distance between Na-Na atom does not alter on alloying. Like Na-Na, the effective interaction between Cd-Cd atom (figure 2) becomes smaller at compound forming concentration in comparision to $Cd_{0.5}$ $Na_{0.5}$ alloys. The position of $\Phi_{Cd\text{-}Na}$ (figure 3) is found to be intermediate between exhibit the maximum tendency of effective interaction between $\Phi_{Na\text{-}Na}$ and $\Phi_{cd\text{-}cd}$. The (figure 3) also shows the effective interaction between Cd-Cd atoms is greater than that of Na-Na atoms in $Cd_{0.66}$ $Na_{0..34}$ alloys.

1.4. *Hard sphere diameter (σ_i) and entropy of mixing S_M*

The computed pair potentials have been used to determine the hard sphere diameter using eq. (6). The value of r which satisfies eq. (6), is taken as the hard sphere diameter of NaCd liquid alloys. These are tabulated in Table 2.

The slight expansion of hard sphere diameter Cd(σ_{cd}) has been observed at all concentration of Cd, where as the σ_{Na} expands on alloying in the concentration range $0.1 \leq C_{Cd} \leq 0.6$ and starts decreasing beyond this concentration range. The ratio of diameter σ is almost constant i.e. 0.83 to 0.84.

The entropy of mixing S_M of NaCd liquid alloys is computed using eqs. (16) and (25). The hard sphere diameter $\sigma_1$and σ_2 required for the computation are taken from Table 2. The value of σ_3 (hard sphere diameter) of the complex is fixed by adjusting its value through eq. (25), so that the good fit for experimental values is obtained. σ_3 for NaCd system thus evaluated are found to be and 6.56 at 673K. However, Ψcomp. appearing in eq. (24) can be evaluated from the work Hertzberg [23] but due to complexities in the determination we have treated it as parameter and fixed it as Ψcomp. (21.0K_B) for NaCd liquid alloys. The computed and experimental values of Hultgren et al.[24] of entropy of mixing of NaCd systems are tabulated in Table 3.

Table 3. Entropy of mixing for NaCd compound forming alloys

Alloys	Temperature	C_{Na}	Theory	Expt.*
NaCd	673K	0.1	0.243	0.244
		0.2	0.370	0.336
		0.3	0.400	0.359
		0.4	0.338	0.321
		0.5	0.136	0.239
		0.6	0.046	0.143
		0.7	0.270	0.053
		0.8	0.840	-0.010
		0.9	0.670	-0.023

*Hultgreen *et al.* 1973[24]

S_M Vs C_{Cd} has been plotted in figure 4, which shows reasonable agreement between the theory and experiment in the concentration range $0.1 \leq C_{cd} \leq 0.6$, beyond this concentration range a distinct deviation is observed. Theoretical values are all positive, whereas the experimental values are slightly negative in the concentration range $0.8 \leq C_{cd} \leq 0.9$.

The disagreement between theory and experiment might be due to parameterisation of σ_3 and Ψcompound, however attempts are being made to improve the theory, so as to give better results.

CONCLUSION

In our theoretical model, we have studied entropy of mixing of NaCd liquid alloys as a function of concentration by using the pseudopotential formalism incorporated with the phenomena of compound formation.The concentration dependent anomaly occurs due to the preferential ordering of unlike atoms as nearest neighbour forming compound like Cd_2Na in the melt. Hence the binary mixture can be treated as a ternary mixture of unassociated constituent atoms and the complex.

The effective interaction between Na -Na atoms decreases on alloying, being minimum for compound forming alloys($Cd_{0.66}$ $Na_{0.34}$). The nearest neighbour distance between Na-Na does not alter. The effective interaction between Cd -Cd atoms decreases from pure to NaCd alloys, being minimum at ($Cd_{0.66}$ $Na_{0.34}$). The nearest neighbour distance between Cd-Cd doesnot alter on alloying.The position of $\Phi_{Cd\text{-}Na}$ is intermediate between $\Phi_{Cd\text{-}Cd}$ and $\Phi_{Na\text{-}Na}$ .The effective interaction between Cd -Cd atoms is greater than that of Na-Na atoms in compound forming alloys.The computed values of S_M are positive at all concentrations for NaCd System. In NaCd system, there is a good agreement between theory and experiment in the concentration range $0.1 \leq C_{Cd} \leq 0.6$, beyond this there is distinct deviation. This might be a happening due to parameterization of σ3 and Ψcomp.

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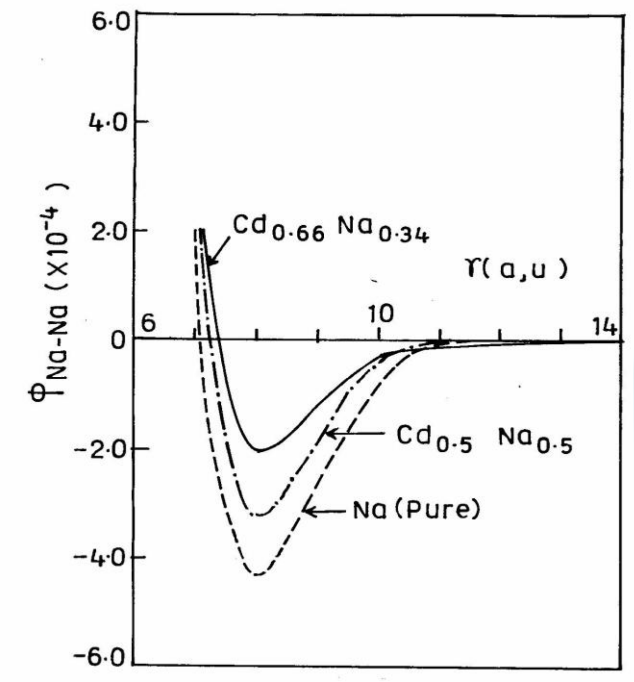

Fig 1: $\Phi_{Na\text{-}Na}$ vs r for NaCd (673K) at different concentrations.

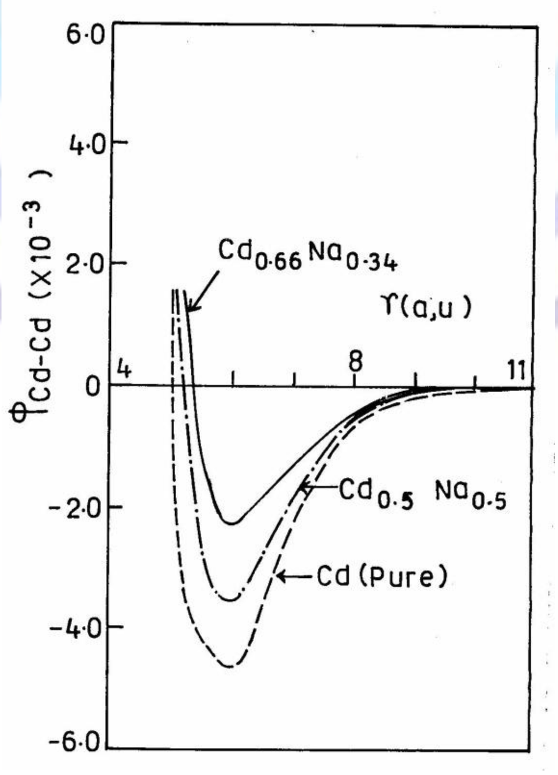

Fig 2: $\Phi_{Cd\text{-}Cd}$ vs r for NaCd (673K) at different concentrations.

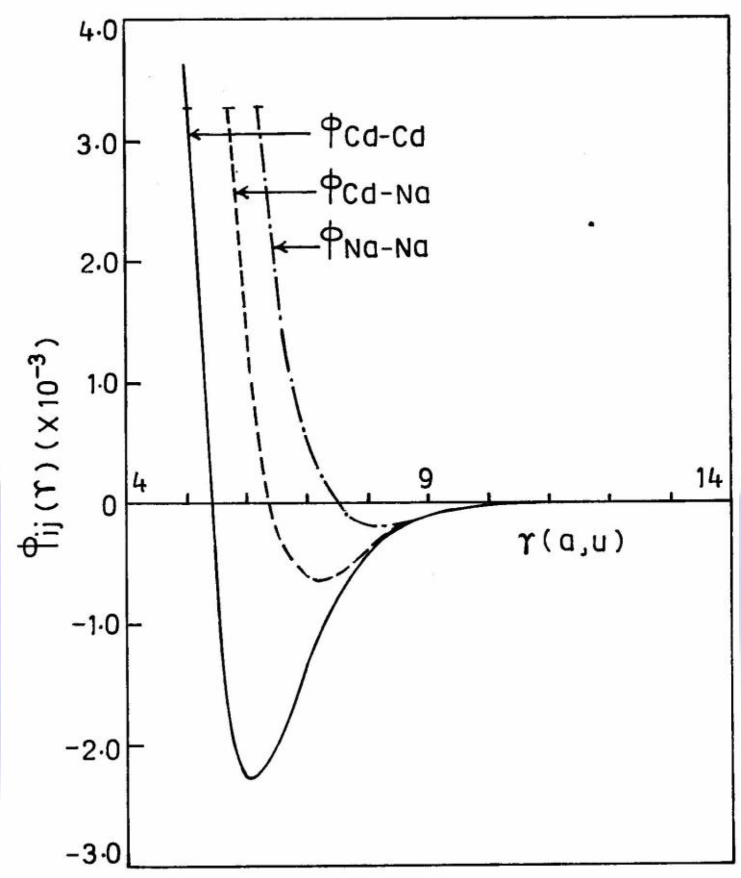

Fig 3: Φ_{ij} Vs r for NaCd(673K) at Ccd=0.66

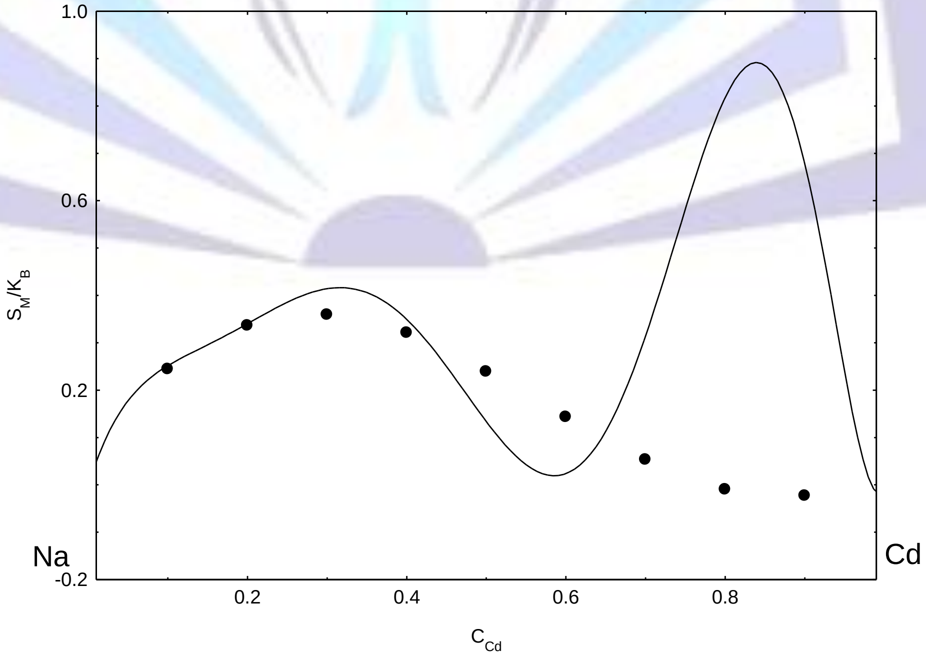

Fig 4: S_M/K_B Vs C_{Cd} for NaCd liquid alloys at 673K. (Closed lines): theory; (closed circles): experiment[24], [25]

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