

Thermophysical Behavior of Sodium Lead Alloy at Different Temperature

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Abstract

Theoretical study of thermophysical properties of binary liquid sodium-lead alloy at temperatures 700 K, 900 K and 1100 K have been analyzed as a function of concentration by considering temperature dependent exponential interaction parameters in the framework of R-K polynomials. The viscosity and surface tension of the alloy have been studied by BBK model and improved derivation of Butler equation respectively. The study provides the information of moderately interacting alloy as well as ordering nature at all concentration of sodium. The viscosity and surface tension of the alloy decrease with increase in temperature.

Keywords: Binary alloys, R-K polynomials, artefact, ordering, segregating

1. Introduction

In metallurgy, the composition and temperature dependent thermophysical study of alloys is one of the crucial tool for designing advanced materials possessing high mechanical strength, heat resistance and chemical resistance. During alloy formation,

there is change in bonding and structural rearrangement of atoms of a given system which make difficult to realize it as compared to the crystals. The mixing property of the alloy is mainly influenced by electrochemical effect, size of atoms and the concentration of constituent elements so that atoms of individual elements either tend to align showing ordering tendency or segregating tendency [1-4]. Thus the understanding of mixing behavior of metals forming alloys has been a great interest to metallurgists and physicists. However, materials remain uninvestigated due to experimental difficulties and time constraint. In order to solve such problem, significant efforts have been done by theoreticians developing different theoretical models [5-9]. The limitation of such models is that they can study different properties of alloys at particular temperature. But the understanding of the behavior of alloys at higher temperatures is essential for various technological applications [10].

The Redlich and Kister (usually known as R-K equation) [11] is often used to understand the mixing properties of the alloys at any higher temperature. The equation is based on the temperature dependence linear interaction parameters known as R-K polynomials. Such polynomials for few alloys are given by Ansara et al. [12] but not sufficient to all alloys. On the other hand, the computed thermodynamic properties by using these polynomials on R-K equation leads to the artificial miscibility gap or artefacts in some binary alloys [13, 14]. Chen et al. [15] concluded that a number of calphad assessments lead to an artefacts (artificial miscibility gap) of binary liquid solutions at higher temperatures. According to Kaptay [16, 17] such artefacts can be removed using exponential temperature dependent interaction parameters instead of linear interaction parameters.

The present work aims to develop temperature dependent exponential interaction parameters based on the R-K polynomials as suggested by Kaptay to remove artifacts and apply these parameters to study the thermophysical properties of sodium lead liquid alloy at temperatures 700 K, 900 K and 1100 K respectively. In the study we use experimental data of Na-Pb alloy at 700 K given by Hultgren et al. [18] in order to compare our result. The viscosity and surface tension of the alloy is studied by Budai-Benko- Kaptay model [19] and improved derivation of Butler equation [20]. But due to lack of experimental result, these are not compared. Being highly reactive, the element sodium easily combines with others and makes complexes and hence the behavior of sodium alloys are deviated from the ideal alloys. This makes it interesting to study the sodium alloys. Sodium lead alloy is one of the important substance used in lead acid batteries as a positive plate and provides many advantages over advanced battery systems [21].

The organization of this paper is as follows. In Section 2, the expressions required for the calculation are presented. In Section 3, result and general discussion of Na-Pb alloy are presented. Finally the conclusions are presented in Section 4.

2. Formalism

The composition dependent excess Gibbs free energy of binary liquid alloy is calculated by R-K equation as [11]

$$\Delta G^{XS} = C_1 C_2 \sum_{i=0}^n K_i (C_1 - C_2)^i \quad (1)$$

Where ΔG^{XS} excess Gibbs energy of binary is alloy, C_1 and C_2 are concentration of the components of the alloy and K_i is temperature dependent linear interaction parameters known as R-K polynomials. It can be expressed as

$$K_i = \alpha_i - \beta_i T \quad (2)$$

Where α_i (J/mol) is the enthalpy like semi-empirical coefficient and β_i (J/mol K) is entropy like semi-empirical coefficient of R-K Polynomials.

From equations (1) and (2),

$$\Delta G^{XS} = C_1 C_2 \sum_{i=0}^n (\alpha_i - \beta_i T) (C_1 - C_2)^i \quad (3)$$

The excess Gibbs free energy of binary liquid alloy is related to the enthalpy (ΔH) and excess entropy of mixing (ΔS^{XS}) by standard relation as

$$\Delta G^{XS} = \Delta H - T \Delta S^{XS} \quad (4)$$

From equations (2), (3) and (4), we get

$$\Delta H = C_1 C_2 \sum_{i=0}^n \alpha_i (C_1 - C_2)^i \quad (5)$$

and

$$\Delta S^{XS} = C_1 C_2 \sum_{i=0}^n \beta_i (C_1 - C_2)^i \quad (6)$$

According to Kaptay [16, 17] the temperature dependent exponential interaction parameters of binary alloy are given as,

$$L_i = \varepsilon_i \exp\left(-\frac{T}{t_i}\right) \quad (7)$$

Where ε_i (J/mol) and t_i (K) are semi-empirical parameters.

Solving equations (5), (6) and (7), the relations for enthalpy and excess entropy of binary liquid alloy are given below.

$$\Delta H = C_1 C_2 \sum_{i=0}^n \left(1 + \frac{T}{t_i}\right) \varepsilon_i \exp\left(-\frac{T}{t_i}\right) (C_1 - C_2)^i \quad (8)$$

$$\Delta S^{XS} = C_1 C_2 \sum_{i=0}^n \frac{\varepsilon_i}{t_i} \exp\left(-\frac{T}{t_i}\right) (C_1 - C_2)^i \quad (9)$$

The activities (a_i) of each components of the alloy are obtained from their respective partial excess Gibbs free energies (G_i^{xs}) as

$$a_i = C_i \exp\left(\frac{G_i^{xs}}{RT}\right) \quad (10)$$

The partial excess Gibbs energy of i^{th} component of alloy is related to the excess Gibbs energy of mixing by the following relation [22].

$$G_i^{xs} = \Delta G^{xs} + \sum_{j=1}^2 (\delta_{ij} - C_j) \frac{\partial(\Delta G^{xs})}{\partial C_j} \quad (11)$$

Where δ_{ij} is the Kronecker delta function.

The local ordering of atoms of alloy can be explained in terms of structural property, the concentration fluctuation in long wavelength limit, which is derived from standard relation as

$$S_{CC}(0) = RT \left[\frac{\partial^2 G_M}{\partial C^2} \right]_{T,P,N}^{-1} \quad (12)$$

Where G_M is Gibbs free energy of mixing.

After finding the relation of Gibbs free energy of mixing (G_M) in terms of interaction parameters and substituting in equation to (12), we get

$$S_{CC}(0) = RT \left[-2L_0 + (-12C_1 + 6)L_1 + (-48C_1^2 + 48C_1 - 10)L_2 + \frac{RT}{C_1 C_2} \right]^{-1} \quad (13)$$

The mixing behavior of binary liquid alloy can be investigated at the microscopic level in terms of viscosity which provides information about atomic transport properties. The viscosity of the alloy by using BBK model is given as

$$\eta = P \left\{ T (C_1 M_1^0 + C_2 M_2^0) \right\}^{\frac{1}{2}} (C_1 V_1^0 + C_2 V_2^0 + V^E)^{\frac{-2}{3}} \times \exp \left\{ \left(C_1 T_{m,1} + C_2 T_{m,2} - \frac{H_M}{qR} \right) \frac{Q}{T} \right\} \quad (14)$$

Where, P and Q are constants whose values are $(1.80 \pm 0.39) \times 10^{-8} (\text{J/Kmol}^{1/3})^{1/2}$ and (2.34 ± 0.20) respectively, q is semi empirical parameter having value equal to 25.4. Similarly $M_i^0, V_i^0, T_{M,i}, V^E$ and R respectively are molar mass, molar volume, effective melting temperature of constituent elements of the alloy ($i=1,2$), excess volume of the alloy and universal gas constant.

According to improved derivation of Butler equation, the surface tension (σ) of binary liquid alloy is given as

$$\sigma = \frac{A_i^0}{A_i} \sigma_i^0 + \frac{RT}{A_i} \ln \frac{C_i^S}{C_i^b} + \frac{G_i^{S,XS} - G_i^{b,XS}}{A_i} \quad (15)$$

Where σ_i^0 and A_i^0 are surface tension, molar surface area of pure liquid metal respectively, A_i is partial molar surface area and is C_i^S surface concentration of i^{th} component. Similarly $G_i^{S,XS}$ and $G_i^{b,XS}$ are partial excess free energy of mixing in the surface and bulk of constituent elements of the alloy respectively. It will be better to mention that $C_1^S + C_2^S = 1$ and $C_1^b + C_2^b = 1$.

The molar surface area of each pure component is given as [23].

$$A_i^0 = gN^{1/3} \left(\frac{M_i^0}{\rho_i^0} \right)^{2/3} \quad (16)$$

Where g , ρ_i^0 and N are geometrical constant, density of each pure element at its melting point, and Avogadro's number respectively. The geometrical constant (g) is expressed as,

$$g = \left(\frac{3f_V}{4} \right)^{\frac{2}{3}} \frac{\pi^{\frac{1}{3}}}{f_S} \quad (17)$$

Where f_V and f_S respectively are volume packing fraction and surface packing fraction. Their values are based on the crystal structure type of every pure component of alloys.

The density and surface tension of individual elements of the alloy at different temperatures are given by following equations [24].

$$\rho_j^0 = \rho_j + \frac{\partial \rho}{\partial T} (T - T_0) \quad (18)$$

$$\sigma_j^0 = \sigma_j + \frac{\partial \sigma}{\partial T} (T - T_0) \quad (19)$$

Where ρ_j , σ_j are density, surface tension of each component at its melting point and T_0 is melting temperature of each component. Similarly $\frac{\partial \rho}{\partial T}$ and $\frac{\partial \sigma}{\partial T}$ are temperature derivatives of density and surface tension respectively.

3. Result and Discussion

The exponential interaction parameters for the liquid Na-Pb alloy are optimized from experimental enthalpy of mixing and excess entropy of mixing [18] in the R-K polynomial framework using equations (7). The optimized temperature dependent exponential interaction parameters are given below.

$$L_0 = -66044.67 \exp(-4.2 \times 10^{-4} T)$$

$$L_1 = -31676.45 \exp(-1.11 \times 10^{-3} T)$$

$$L_2 = -72368.62 \exp(-1.56 \times 10^{-2} T)$$

The exponential parameters thus optimized are used to compute the excess Gibbs energy, enthalpy of mixing and concentration fluctuation in long wavelength limit at 700 K, 900 K and 1100 K. The computed values of excess Gibbs free energy and enthalpy of mixing at 700K are reasonable agreement with experimental values and

these become less negative with increasing temperature as shown in figures (1) and (2). The figures also indicate that the system is moderately interacting at 700 K.

The deviation from the ideal behavior of liquid alloys can be explained by activities, a measure of nature to leave the mixture [25] as the magnitude depends on the interaction of components of the alloy. The equation (10) is used for the theoretical calculation of activities of each component of the alloy. The activities of Na and Pb computed at 700 K, 900 K and 1100 K are shown in figure (3) which indicate that as temperature increases the components try to leave the solution i.e. they try to become less interacting.

The local arrangement of atoms in the alloy can be studied theoretically in microscopic level by the thermodynamical parameters 'concentration fluctuation in long wave limit ($S_{CC}(0)$)'. It is considered as important tool to identify the segregating or ordering nature of the alloy [19]. For a given concentration if $S_{CC}(0) > S_{CC}^{id}(0)$, the alloy has segregating nature while $S_{CC}(0) < S_{CC}^{id}(0)$ indicates the ordering nature [26]. The plot of $S_{CC}(0)$ at different concentrations of sodium and at different temperatures along with ideal values is shown in figure (4).

The figure shows that the theoretical value of $S_{CC}(0)$ lies below the ideal value of $S_{CC}(0)$ at all concentration of Na and at all temperatures and hence the alloy shows ordering nature but the ordering nature of the alloy decreases with increase in temperature.

To compute the theoretical value of viscosity of the alloy at different temperature we use equation (14). The molar volume of each component of the alloy at different temperature is determined by computing the densities at respective temperatures. The values of densities of each component at temperatures 700 K, 900 K, and 1100 K are obtained from relation for different temperature by the help of equation (18). Due to lack of experimental value, the excess molar volume (V^E) is taken as zero. In fact, the value of V^E is non-zero for non-ideal alloy but contribution of this term is too small. [19, 27]. The viscosity of the alloy decreases with the increase in temperature as shown in the figure (5).

To calculate the surface tension of Na – Pb alloy the density and surface tension of individual metals are calculated at different temperatures 700 K, 900 K and 1100 K by using relations (18) and (19) respectively. The bulk excess free energy of individual sodium and lead in liquid state at aforementioned temperatures are obtained by using equation (11). The geometrical structure factor (g) and ratio of surface excess free energy to the bulk excess free energy ($\beta = \frac{G_j^{s,xs}}{G_j^{b,xs}}$) are considered 1.061 and 0.818 [28]

respectively. In the case of negligible excess molar volume (V^E) of the alloy, the molar volume of pure component can replace the partial molar volume. In such situation the partial surface area (A_i) is obviously replaced by surface area (A_i^0) of the same pure component [20, 29]. Thus writing these values to the both metals in equation (16) and solving them simultaneously, we obtain surface concentrations of both metals and then

using such surface concentration of corresponding metals, the surface tension of the alloy is obtained. The computed surface concentration of sodium and surface tension of the alloy versus concentration of sodium are shown in figures (6) and (7) respectively.

Figure (6) tells that the surface concentration of sodium increases with its increase in concentration but it decreases with increase in temperature because another component i.e. lead gets energy and tries to vibrate or move towards the surface at higher temperatures. Similarly in the figure (7) the surface tension of the liquid alloy decreases with increase in temperature which is usual behavior.

4. Conclusion

The conclusions drawn from the study are given below.

1. The excess Gibbs free energy, enthalpy, activity and concentration fluctuation in long wave limit at 700 K are reasonable agreement with experimental values.
2. The alloy is moderately interacting and interacting tendency decreases with increase in temperature.
3. It is completely ordering at temperature 700 K, 900 K and 1100 K but goes towards less ordering with increase in temperature.
4. The sodium atoms segregates on the surface at 700 K but surface segregation of sodium decreases with increase in temperature of the alloy.
5. The viscosity and the surface tension of the alloy decrease with increase in concentration of sodium in the alloy and both decrease with increase in temperature.

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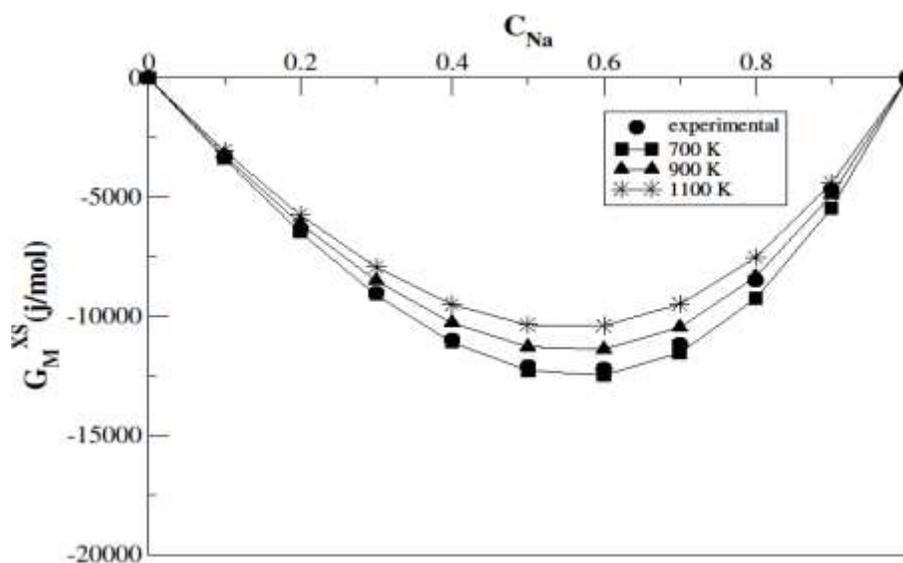
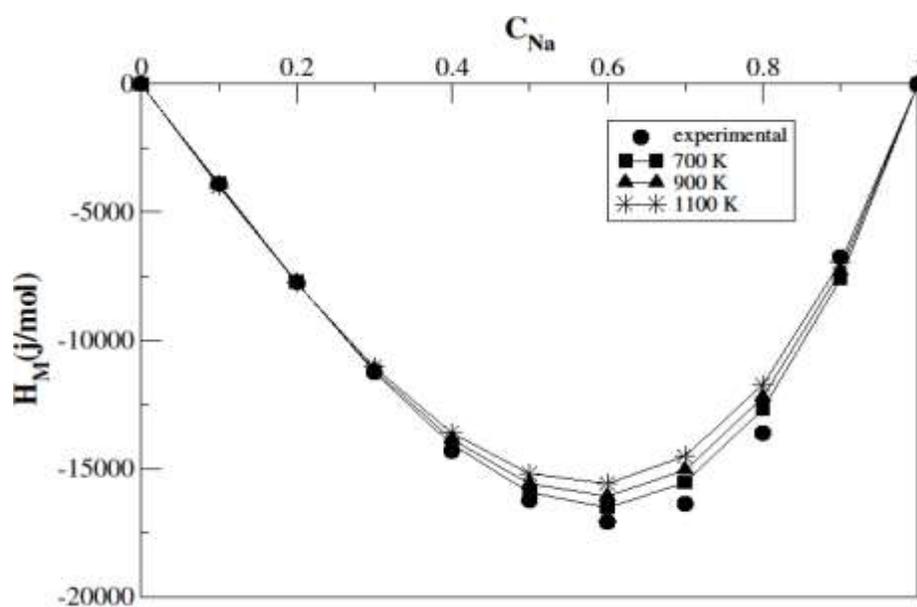
Figure 1. Excess Gibbs free energy vs. concentration of Na**Figure 2.** Enthalpy of mixing vs. concentration of Na

Figure 3. Activity vs. concentration of Na

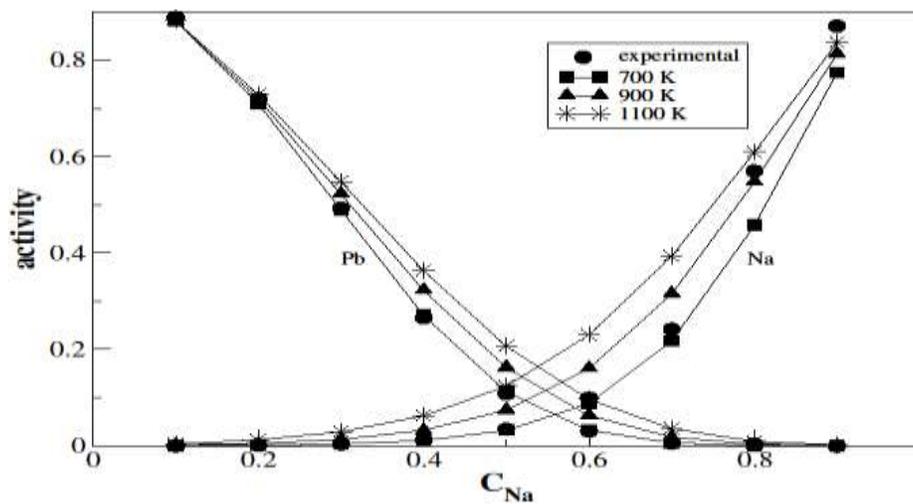


Figure 4. Concentration fluctuation in long wavelength limit vs. concentration of Na

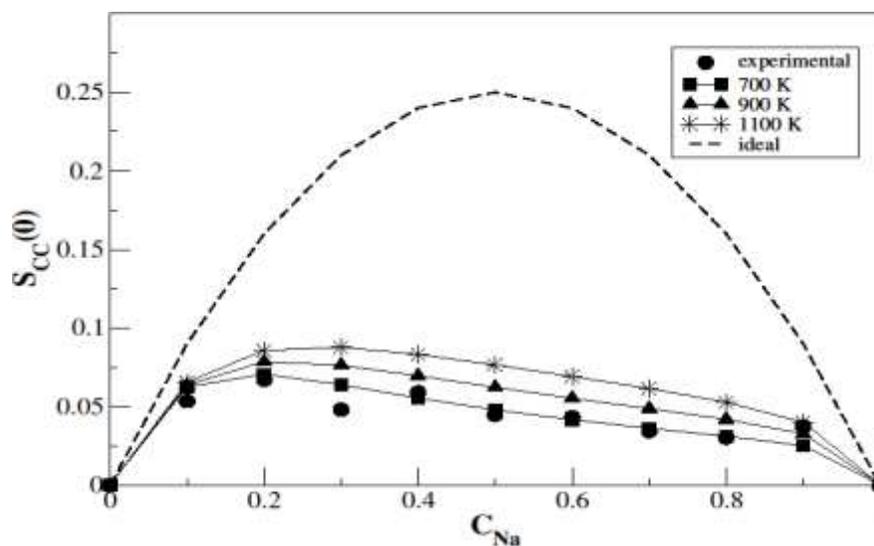


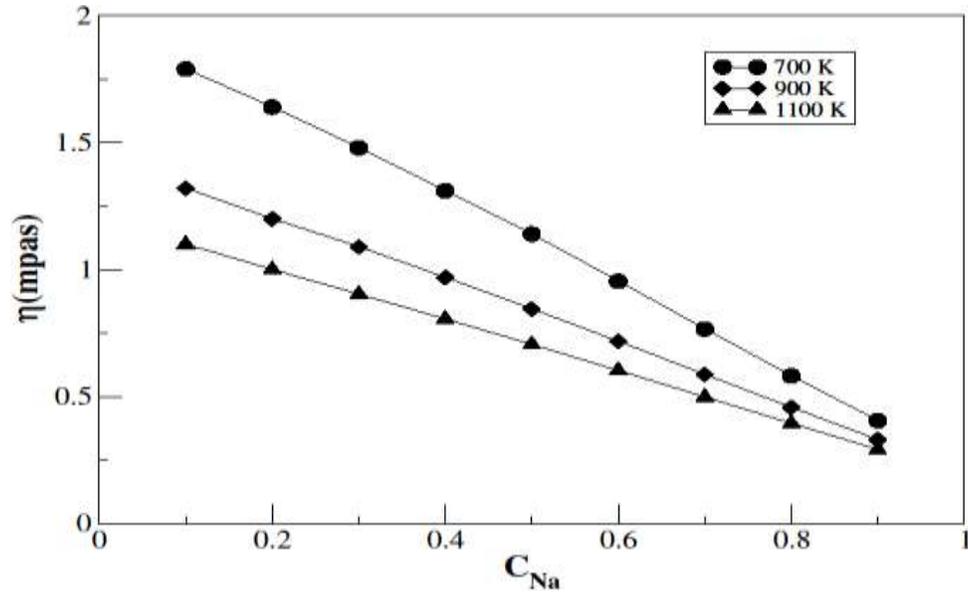
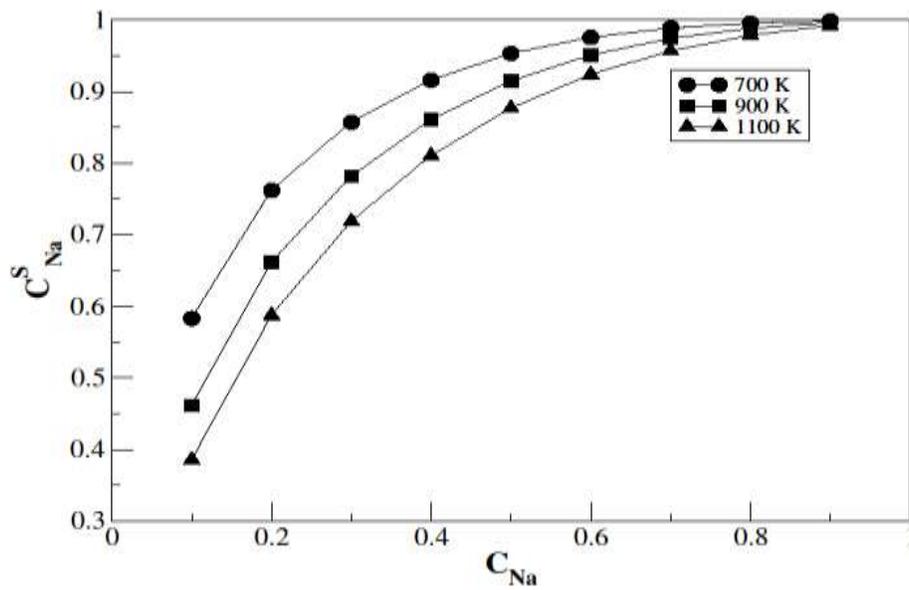
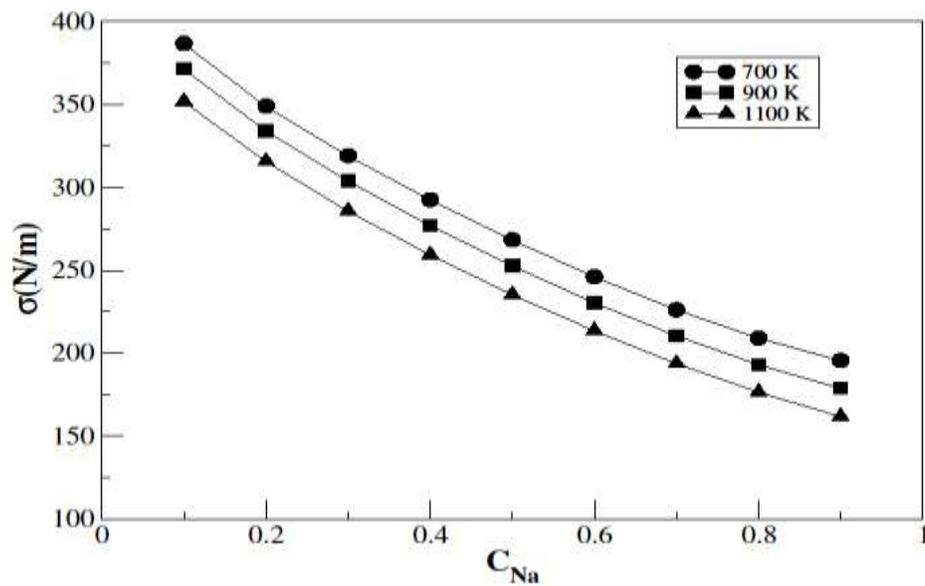
Figure 5. Viscosity vs. concentration of Na**Figure 6.** Surface segregation vs. concentration of Na

Figure 7. Surface tension vs. concentration of Na



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