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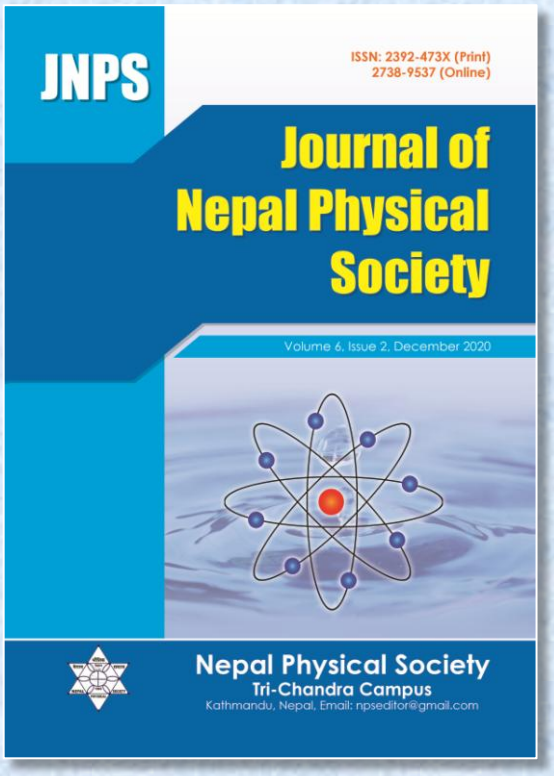

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High Temperature Assessment of K-Tl Binary Liquid Alloy

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Abstract

Theoretical study of thermodynamic properties of binary liquid Potassium-Thallium alloy at temperatures 798 K, 1000 K, 1200 K and 1400 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 as well as segregating nature at the low concentration of Thallium and ordering nature at high concentration of Thallium and the viscosity and surface tension of the alloy decrease with increase in temperature.

Keywords: Exponential interaction parameters; R-K Polynomial; Ordering nature; Artefact.

1. INTRODUCTION

Traditional models of binary liquid alloy [1-4] can give the information of different properties of the alloys near their melting temperature and the model that provides information of the thermodynamic properties of alloys near melting temperature may not necessarily predict these properties at other higher temperatures. On the other hand the various properties of the alloys in liquid state are studied in metallurgy for high temperature applications.Thus the knowledge of mixing nature of components forming alloys at higher temperatures is considered a great interest to the metallurgical science. However, the investigation of alloys remains incomplete due to time constraint as well as experimental difficulties at all temperatures.

Generally the Redlich – Kister equation [5] is used for the understanding of thermodynamic behavior of binary alloy at higher temperatures which is mainly based on the temperature dependent linear interaction energy parameters (which are often known as R-K polynomials) and hence the temperature dependent linear interaction parameters of different alloys have been developed [6] for the theoretical investigation of liquid alloys at different temperatures. However there arises miscibility gap (artefact or T-artefact) in some binary alloys during the study of different properties at higher temperatures using such linear interaction parameters [7, 8]. In order to remove such artefact different attempts have been done. Mainly two models are proposed within the framework of R-K polynomials; exponential model [9] and extension of linear model by exponential term [10]. According to the exponential model the interaction parameters are exponentially dependent on temperature and are effective to remove artificial miscibility gap caused by the linear interaction parameters. Similarly the second model which is usually denoted by "LET function" contains linear as well as exponential terms with four semi empirical parameters but two of them are fixed for all binary systems. It claims that the exponential model can lead to a low –T artefact [11].

The present work aims to develop temperature dependent exponential interaction parameters in the frame work of R-K polynomials according to model given by Kaptay [9] and use them to study the thermodynamic, structural, transport (viscosity) and surface properties (surface tension and surface concentration) of K-Tl liquid alloy at temperatures 798 K, 1000 K, 1200 K and 1400 K respectively. The computed values of excess Gibbs free energy

of mixing, enthalpy of mixing, concentration fluctuation in long wave length limit and activity of each component at 798 K are compared with available experimental values [12]. Similarly surface tension and the viscosity at afore mentioned temperatures are studied by the improved derivation of the Butler equation [13] and BBK (Budai-Benko-Kaptay) model [14]. Due to lack of experimental values, the result of latter two models cannot be compared.

Theoretical basis

The relationship between the excess Gibbs free energy (ΔG^{XS}), enthalpy (ΔH) and excess entropy of mixing (ΔS^{xs}) of binary liquid alloy is given by standard relation as

$$\Delta G^{XS} = \Delta H - T\Delta S^{xs} \quad \text{.....(1)}$$

The Gibbs free energy of binary liquid alloy is calculated by R-K equation as [5]

$$\Delta G^{XS} = C_1 C_2 \sum_{i=0}^{n} K_i \, (C_1 - C_2)^i \text{ .....(2)}$$

WhereC_1 and C_2 are concentration of the components of the alloy and K_i is ith temperature dependent linear interaction parameter between two components of alloy known as R-K polynomial. It can be expressed as

$$K_i = a_i - b_i T \text{ .....(3)}$$

Where a_i (J/mol) the enthalpy is like semi-empirical coefficient and b_i(J/mol K) is entropy like semi-empirical coefficient of R-K Polynomials. From equation (2) and (3),

$$\Delta G^{XS} = C_1 C_2 \sum_{i=0}^{n} (a_i - b_i T) \, (C_1 - C_2)^i \text{ .....(4)}$$

Comparing equations (1), and (4), we get

$$\Delta H = C_1 C_2 \sum_{i=0}^{n} a_i \, (C_1 - C_2)^i \text{ .....(5)}$$

and

$$\Delta S^{xs} = C_1 C_2 \sum_{i=0}^{n} b_i \, (C_1 - C_2)^i \text{ .....(6)}$$

According to Kaptay [9, 11] the temperature dependent exponential interaction parameters of binary alloy are given as,

$$K_i = h_i \exp\left(-\frac{T}{t_i}\right) \text{ .....(7)}$$

Where h_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.

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

$$\Delta S^{xs} = C_1 C_2 \sum_{i=0}^{n} \frac{h_i}{t_i} \exp\left(-\frac{T}{t_i}\right) \; (C_1 - C_2)^i \text{.....(9)}$$

The activities (a_i) of components of the alloy are related to their respective partial excess Gibbs energies (G_i^{xs}) as [15]

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

The partial excess Gibbs energy of i$^{\text{th}}$ component of alloy is related to the Gibbs energy of mixing by the following relation [16].

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

Where, δ_{ij} is Kronecker delta function.

The structural behavior of alloy can be theoretically explained in terms of the concentration fluctuation in long wavelength limit ($S_{CC}(0)$) which is derived from standard relation as [17]

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

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

$$S_{CC}(0) = RT \left[\frac{RT}{C_1 C_2} - 2K_0 + (-12C_1 + 6)K_1 + (-48C_1^2 + 48C_1 - 10)K_2\right]^{-1} \text{ .....(13)}$$

The value of $S_{CC}(0)$ can be obtained by using experimental observed activities with the help of following equation (14). Hence, the values of

$S_{CC}(0)$ obtained from this equation are called as experimental values.

$$S_{CC}(0) = C_1 a_1 \left[\frac{\partial a_1}{\partial C_1}\right]^{-1}_{T,P,N} = C_2 a_2 \left[\frac{\partial a_2}{\partial C_2}\right]^{-1}_{T,P,N} \quad .....(14)$$

The mixing nature of molten alloy can also be studied at the microscopic level in terms of viscosity which gives idea about atomic transport properties. The viscosity of the alloy is studied by using BBK model which is given as

$$\eta = A\{T\,(C_1 M_1^0 + C_2 M_2^0)\}^{\frac{1}{2}}\,(C_1 V_1 + C_1 V_2 + V^E)^{\frac{-2}{3}} \times \exp\left\{\left(C_1 T_{m,1} + C_2 T_{m,2}\frac{H_M}{qR}\right)\frac{B}{T}\right\} \quad .....(15)$$

Where, A and B are constants whose values are $(1.80 \pm 0.39) \times 10^{-8}$ and (2.34 ± 0.20) respectively, q is semi empirical parameter having value equal to 25.4.Similarly M_i^0, V_i ,$T_{m,i}$, V^E and R respectively 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.

The surface tension (σ) of binary alloy is given by the improved Butler equation as

$$\sigma = \frac{S_i^0}{S_i}\sigma_i^0 + \frac{RT}{S_i}\ln\frac{C_i^S}{C_i^b} + \frac{G_i^{S,XS} - G_i^{b,XS}}{S_i} \quad .....(16)$$

Where $\sigma_i^0 S_i^0, S_i$ are surface tension of pure liquid metal, molar surface area of pure liquid metal and partial molar surface area of component i respectively. $G_i^{S,XS}$and $G_i^{b,XS}$ are partial excess free energy of mixing in the surface and bulk of constituent elements of the alloy respectively.

The molar surface area of pure component i is given as [18].

$$S_i^0 = \chi\left(\frac{M_i^0}{\rho_i^0}\right)^{2/3} \mathrm{Nav}^{1/3} \quad .....(17)$$

Where M_i^0, ρ_i^0, χ and N_{av} are geometrical constant, molar mass , density of each pure element at its melting point, geometrical constant and Avogadro's number respectively. The value of geometrical constant is expressed as,

$$\chi = \left(\frac{3f_V}{4}\right)^{\frac{2}{3}}\frac{\pi^{\frac{1}{3}}}{f_S} \quad .....(18)$$

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

The density and surface tension of each pure component of the alloy at temperature T are expressed as [19],

$$\rho_i^0 = \rho_i + \frac{\partial \rho}{\partial T}(T - T_0) \quad .....(19)$$

$$\sigma_i^0 = \sigma_i + \frac{\partial \sigma}{\partial T}(T - T_0) \quad .....(20)$$

Whereρ_i, $\sigma_{i,}$ T_0 are density, surface tension of each component at its melting point and melting temperature of each component respectively. 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 temperature dependent exponential interaction parameters are optimized for liquid K-Tl alloy from the observed values of enthalpy of mixing and excess entropy of mixing [12] in the framework of R-K polynomials using equations (3) and (7). The parameters thus obtained are given in the following table (1).

Table 1: The optimized temperature dependent exponential interaction parameters of liquid K-Tl alloy.

parameter	K_0	K_1	K_2
exponential	-46405.3exp(-7.78x10^{-4}T)	-13854.5exp(-6.72x10^{-5}T)	-27718.38exp(2.26x10^{-3}T)

The exponential interaction parameters optimized in this way are used to compute the excess Gibbs energy, enthalpy and concentration fluctuation in long wavelength limit of mixing at 798 K, 1000 K, 1200 K and 1400 K. The computed value of excess Gibbs energy of mixing at 798 K is good

agreement with experimental result whereas enthalpy of mixing at 798 K is reasonable agreement with experimental value. But both become less negative with increase in temperature as shown in figures 1 and 2.

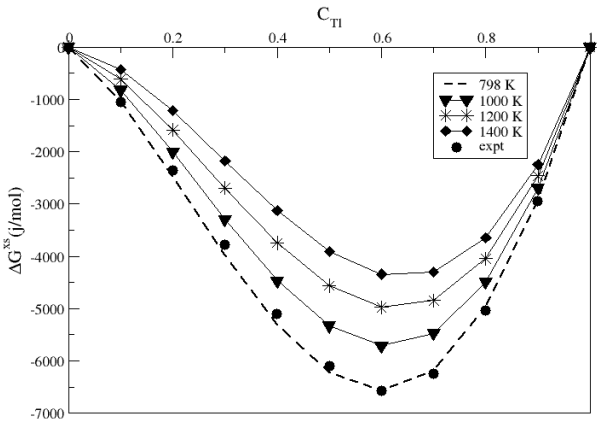

Fig. 1: Excess Gibbs free energy of mixing versus concentration of Tl of liquid binary K-Tl alloy.

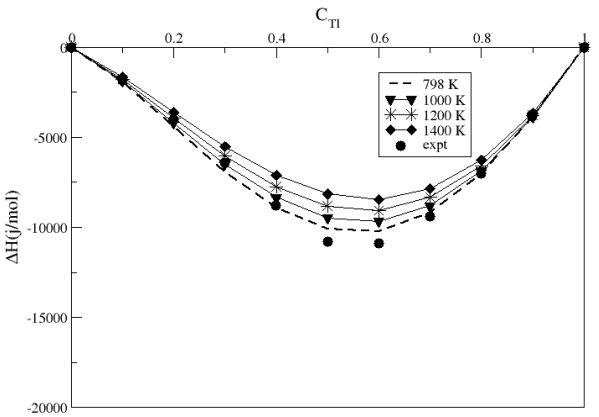

Fig. 2: Enthalpy of mixing versus concentration of Tl of liquid binary K-Tl alloy

The concentration fluctuation in long wave limit ($S_{CC}(0)$) is considered as one of the important Functions for the study of nature of atomic arrangement of the binary liquid as it removes difficulties in the diffraction experiment [17]. For a given concentration if $S_{CC}(0) < S_{CC}^{id}(0)$, the alloy has complex formation nature while $S_{CC}(0) > S_{CC}^{id}(0)$ indicates the segregating nature. The theoretical values of $S_{CC}(0)$ at different concentrations of thallium using exponential interaction parameters is obtained from equation (13). The plot of theoretical along with ideal values of $S_{CC}(0)$ versus concentration of Tl is shown in figure (3).

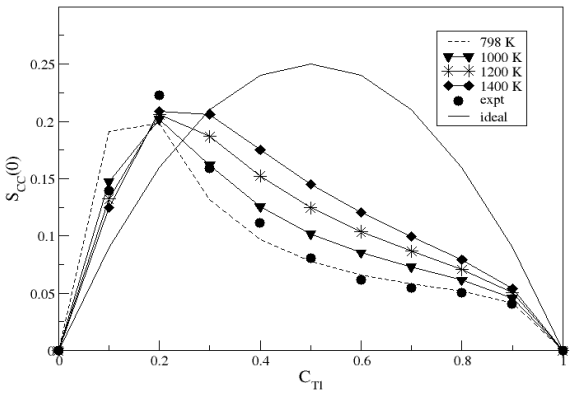

Fig. 3: Concentration fluctuations in long wave limit versus concentration of Tl of liquid binary K-Tl alloy

The figure shows that the theoretical value of $S_{CC}(0)$ lies above ideal value of $S_{CC}(0)$ about 0.25 concentration of thallium at all temperatures and hence the alloy shows segregating nature within this concentration but it lies below ideal value of $S_{CC}(0)$ beyond 0.25 concentration of thallium, which is the indication of ordering nature of the alloy but the segregating and ordering tendency of the alloy try to change with increase in temperature.

The partial excess Gibbs energy of each component computed by equation (11) is used to find the activity of each component in equation (10). The activities of components K and Tl computed by using exponential interaction parameters at temperature 798 K, 1000 K, 1200 K and 1400 K are shown in figure 4.

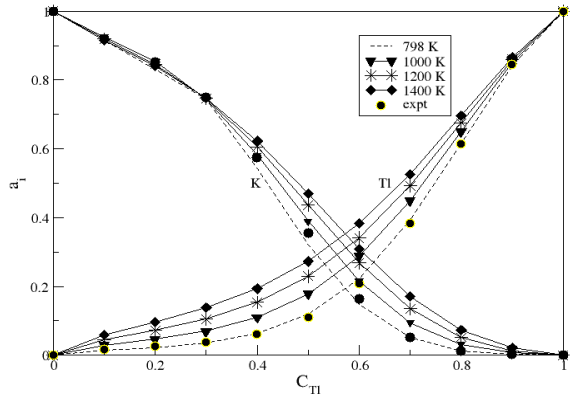

Fig. 4: Activity versus concentration of Tl of liquid binary K-Tl alloy

The equation (15) is used for the theoretical value of viscosity of the alloy at different temperatures. The molar volume of each component of the alloy at different temperatures is determined by computing the densities at respective temperatures. The values of densities of each component at aforementioned temperatures are found from relation given in equation (19). Due to lack of experimental value, the excess molar volume (V^E) is taken as zero. The viscosity of the alloy decreases with the increase in temperatures as shown in the figure 5.

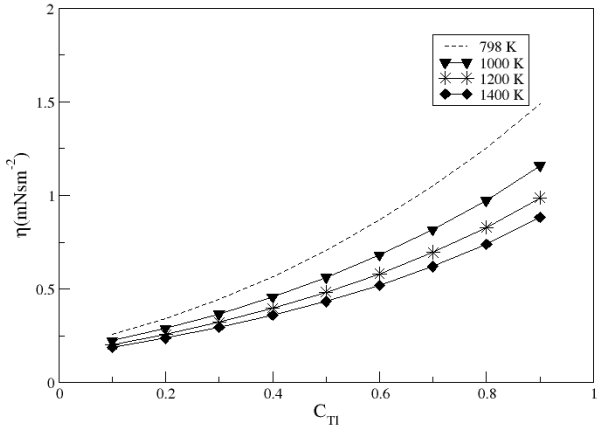

Fig. 5: Viscosity versus concentration of Tl of liquid binary K-Tl alloy

To calculate the surface tension of $K-Tl$ alloy the surface tension of individual metals are calculated at different temperatures by using equation (20). The bulk excess free energy of individual potassium and thallium in liquid state at above temperatures are obtained by using equation (11). The geometrical structure factor and ratio of surface excess free energy to the bulk

Excess free energy ($\frac{G_i^{s,xs}}{G_i^{b,xs}}$) are considered 1.061 and 0.818 respectively [19, 20]. In the case of negligible or unknown excess molar volume of the mixture, the partial molar volume is replaced by the molar volume of same component so that the partial surface area (S_i) is obviously replaced by surface area (S_i^0) of the same pure component [21-23].

Now writing these values to both metals in equation (15) and solving them simultaneously, we first obtain surface concentrations of both metals and then using each surface concentration of corresponding metals, the surface tension of the alloy is obtained. The plots of surface concentration of thallium and surface tension of the alloy versus concentration of thallium are shown in figures (6) and (7) respectively.

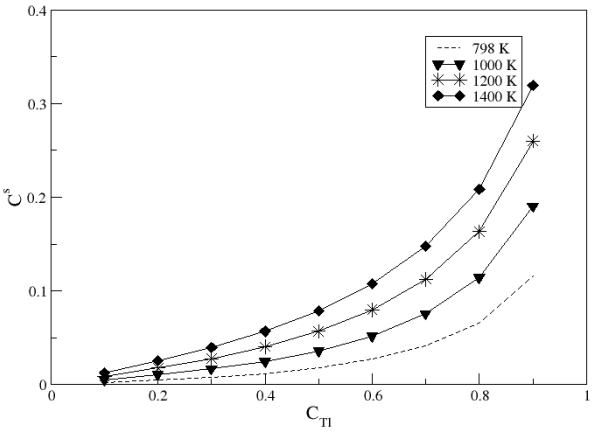

Fig. 6: Surface concentrations versus concentration of Tl of liquid binary K-Tl alloy

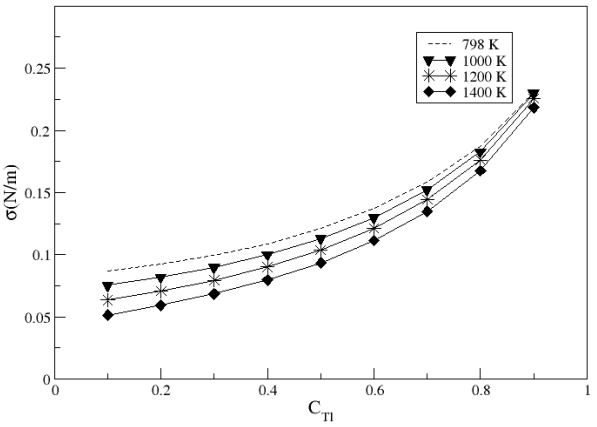

Fig. 7: Surface tension versus concentration of Tl of liquid binary K-Tl alloy

Figure (6) tells that the surface concentration of thallium increases with its increase in concentration and also increases with increase in temperature because it has higher density than potassium. As it gets energy it 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 present study is the theoretical analysis for the understanding of thermodynamic behavior of binary liquid K-Tl alloy at 798 K, 1000 K, 1200 K

and 1400 K by using temperature dependent exponential interaction parameters in the framework of R-K polynomials. The theoretical study shows that the alloy exhibits segregating tendency below about 0.25 concentration of Tl and order tendency above about 0.25 concentration of Tl at all temperatures which become weaker with increasing temperature. The viscosity and surface tension of the alloy decrease with the increase in temperature which are usual behavior of materials.

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