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Determination of surface tension of liquid ternary Ni–Cu–Fe and sub-binary alloys

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ABSTRACT

Experimental data in the literature are almost limited to determine the thermophysical properties of multicomponent complex alloys, especially due to the inability of laboratories to achieve the desired ideal conditions, due to the difficulty of protection from oxidation at high temperatures and other contamination at high temperatures, due to time and cost in laboratory studies. Due to these reasons, the theoretical data obtained in this subject is of great importance. In this study, a series of geometric and physical models, such as Chou's general solution model (GSM), Muggianu's Model, Kohler's Model, Toop's Model, Hillert's Model, Guggenheim's Model, Butler's Model, Egry's Model and ideal solution model for quasi-binary alloy system for Section A: $\text{Ni}_{0.4(1-x)}\text{Cu}_x\text{Fe}_{0.6(1-x)}$ and Section B: $(\text{Ni}_x\text{Cu}_{0.2}\text{Fe}_{0.8-x})$ are used to calculate the surface tension-composition and surface tension-temperature curves of the Cu–Fe–Ni ternary liquid system are plotted. The data for this process is evaluated by means of an extended Redlich-Kister-Muggianu polynomial fit to the experimental values of the surface tensions of the binary liquid alloy systems. The obtained results for these models are also compared with the available data in the literature and relatively good agreements are observed. In addition, the surface segregation having important key factor in determining surface tension of the liquid alloy Ni–Fe–Cu has also been investigated in this work.

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1. Introduction

Surface tension is a fundamental thermophysical property in science and technology, and the precise information about it is also very important for technological and scientific applications. It is a basic parameter in the field of casting and welding operations and it is also widely used in the wetting process.

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It is obvious that the measurement of the surface tension of molten metals at high temperatures is difficult due to the reactivity of the crucibles with the atmosphere. So, the obtained data are diverged from the real values. The precise information about surface tension has an extremely large importance for scientific applications. For this reason, the information obtained from experiments must also be accurate.

Recently, we have published a series of papers concerning the surface tension of the binary, ternary and quaternary alloys. The surface tensions of the liquid $\text{Cu}_x\text{-In}_y\text{-Sn}_z$ alloys have been investigated by geometric models and the Butler for the cross section $\text{Cu}_x\text{-In}_y\text{-Sn}_z$ ($z/(y+z) = 0, 0.1, 0.3, 0.5, 0.7, 0.9, 1$) at 1073 K [1,2]. In another study, the surface tensions of some Pb-free solder systems such as Ag–Bi–Sn [3,4] with cross-sections $\text{Ag/Bi} = 1/1, \text{Ag/Bi} = 1/2, \text{Ag/Bi} = 2/1$, In–Sn–Zn [1,5] with cross-sections $\text{Sn/In} = 1/1, \text{Sn/In} = 1/3$ and $(\text{Ag}_7\text{Cu}_3)_{100-x}\text{Sn}_x$ [1,6] with cross-section $\text{Ag/Cu} = 7/3$ are calculated from the sub-binary surface tension data using the models such as Muggianu's Model, Kohler's Model's Model, Toop's Model, Butler's Model's Model and Chou's General Solution Model (GSM) at some temperatures such as 873, 923 and 1073 K.

The surface tension data for the liquid binary alloys Ag–Bi, Bi–Sn, Ag–Sn and In–Sn have been measured and reported by many authors [7–11]. On the other hand, Eyring's model has been used to calculate the surface tension of liquid Ga–Bi, Ga–Sn, Ga–In [12], Ag–Au [13] and Cu–Ti [14] binary alloys. The surface tensions of liquid Sn–X (X = Ag, Cu) alloys were measured by the constrained drop method in the temperatures between 700 and 1500 K across whole composition range [15]. In the studies [16–19] on the surface tension of Ag–Cu alloy, the authors have compared the calculated values of surface tensions (which are based on Butler's equations) and the experimental data obtained by various researchers. The surface tension and density of Sn–In [20], Sn–Zn [10], and In–Zn [21] alloys in the studies mentioned above concerning the ternary alloys have been reported in related references. Surface tension of In–Sn system was also studied by Novakovic et. al. [11], while surface tension of Sn–Zn system was studied by Kucharski [22].

The surface tensions of the pure elements have been compiled by the Ref. [23] and recently updated by the researchers in Ref. [24]. Density and surface tension data for pure liquid metals, measured by Electromagnetic Levitation were given in details in Ref. [25].

Surface tensions of binary metallic alloys have been calculated several times using Butler's equation. In particular, Tanaka and Iida used to calculate surface tension of a number of binary Fe-based metal alloys [26].

Although there have been only a limited number of experimental data related to surface tension of the binary sub-systems [25, 27–34] and the liquid ternary

Ni–Cu–Fe alloys [34,35] in the literature so far, there are numerous experimental data for the unary systems [23–25,36].

In the last decade, the thermophysical properties of the superalloys have been analysed and interpreted by means of different thermodynamic models [37,38].

Recently, the analytic thermodynamic equations have been developed to calculate the surface tensions of alloys. The lack of experimental data obtained in thermodynamics was compensated for calculated values, provided by reliable models exist in literature. Some of those are: the symmetric geometric model (Muggianu's Model [39], Kohler's Model [40]), asymmetric models (Toop's Model [41] Hillert's Model [42]), Chou's general solution model [43], Guggenheim's Model [44], ideal solution model for quasi-binary system [35] and Butler's Model [45].

The aim of this study is to estimate the surface tension of the fluid alloy ternary Ni–Cu–Fe from surface tension binary systems measured at 1800 K with some important models commonly used in the literature. The excess surface tension values of the three sub-binary systems for the binary alloys Ni–Fe, Ni–Cu, and Cu–Fe were calculated using the classic Redlich–Kister polynomial and were fitted to the accurate experimental surface tension values in literature [25,27–29]. Then, the models mentioned above were considered to calculate the surface tension-composition curves of the Cu–Fe–Ni ternary liquid system. The surface tension model based on Egry's Model [46,47] was also used to compare the surface tension values of these alloys with the values obtained from models mentioned above. The surface tension values are calculated from measured viscosity values of this alloy [34]. The aim of this study is to carry out the calculations of the surface tension of liquid Ni–Cu–Fe alloys using geometric and calphad models.

On the other hand, recently, the density and surface tension [25] of the liquid Cu–Ni–Fe alloy systems have been studied to investigate the behaviour of the mixture. It is mentioned above that, the experimental studies on thermo-physical properties for the Cu–Ni–Fe system are still rare. Generally speaking, the evaporation of some metals at relatively high temperatures could make the experimental measurements difficult and expensive. Taking into account the difficulties mentioned above, we apply the geometrical models in this study to predict the surface tension of the liquid Cu–Ni–Fe ternary alloy system which is composed of the transition metals, such as Cu–Ni, Cu–Fe, and Ni–Fe sub-binary systems. Moreover, it can also be understood from the number of studies in the literature, that there are only a few theoretical studies about excess surface tension, excess viscosity and excess activation energy dealing with Fe-based alloys [48–50]. The number of studies in which the Redlich–Kister parameters that accompany these quantities are too few. Therefore, this study, which is used to determine the Redlich–Kister parameters of the

surface tension of Fe-based Ni–Cu–Fe alloys, aims to create a database for future studies.

2. Some models dealing with surface tension of liquid alloys

The fact that many equations have been developed suggests that a simple single equation cannot identify all existing system types. Some of the many equations related to the surface tension developed in the literature are briefly summarised below.

To determine the surface tensions of binary alloys, it is appropriate to use excess surface tension instead of excess thermodynamic properties. The excess surface tension, γ^E , can be written as follows:

$$\gamma^E = \gamma - \gamma^j \quad (1)$$

where γ is the surface tension of a binary liquid alloy system and γ^j is the surface tension of the ideal solution. This expression for binary alloys can be obtained using the following equation:

$$\gamma = X_1 \gamma_1 + X_2 \gamma_2 \quad (2)$$

where X_i ($i = 1$ and 2) are the mole fractions of the components i, j and γ_i is the surface tension of pure liquid metal in a binary liquid solution.

2.1. GSM model

The most attractive model is GSM which covers the symmetric and asymmetric models and discards the other traditional models. Its expression for surface tension associated with ternary system can be written as a function of the binary and ternary compositions as follows:

$$\begin{aligned} \gamma^E = & [x_1 x_2 / X_{1(12)} X_{2(12)}] \gamma_{12}^E + [x_3 x_1 / X_{3(31)} X_{1(31)}] \gamma_{31}^E \\ & + [x_2 x_3 / X_{2(23)} X_{3(23)}] \gamma_{23}^E \end{aligned} \quad (3)$$

where x_1, x_2 and x_3 are the mole fractions of components i in the ternary alloy, and $X_{1(12)}, X_{3(31)}$ and $X_{2(23)}$ are the mole fractions of components i in the i, j binary system. Here, the binary excess surface tension for binary alloy system is written as

$$\gamma_{ij}^E = X_i X_j \sum_{k=0}^k A_{ij}^k (x_i - x_j)^k \quad (4)$$

The expressions $X_{1(12)}, X_{3(31)}$ and $X_{2(23)}$ can be calculated from the following equations:

$$X_{1(12)} = x_1 + \xi_{12} x_3, \quad X_{2(23)} = x_2 + \xi_{23} x_1 \text{ and } X_{3(31)} = x_3 + \xi_{31} x_2 \quad (5)$$

where ξ is called similarity coefficient and can be expressed as follows:

$$\xi_{12} = \eta_1/(\eta_2 + \eta_1), \quad \xi_{31} = \eta_3/(\eta_3 + \eta_1) \text{ and } \xi_{23} = \eta_2/(\eta_2 + \eta_3) \quad (6)$$

The terms η_1 , η_2 and η_3 in Equation (6) are called the deviation sum of squares and are calculated from the following equations

$$\eta(ij, ik) = \int_0^1 (\gamma_{ij}^E - \gamma_{jk}^E)^2 dX_i \quad (7)$$

where η_1 , η_2 and η_3 are defined as

$$\begin{aligned} \eta_1 &= \int_0^1 (\gamma_{12}^E - \gamma_{13}^E)^2 dX_1 \\ \eta_2 &= \int_0^1 (\gamma_{21}^E - \gamma_{23}^E)^2 dX_2 \\ \eta_3 &= \int_0^1 (\gamma_{31}^E - \gamma_{32}^E)^2 dX_3 \end{aligned} \quad (8)$$

Recently, a general relation has been derived which allows us to calculate of any ternary system [51,52]:

$$\begin{aligned} \eta(ij, ik) &= \sum_{l=0}^n \frac{1}{2(2l+1)(2l+3)(2l+5)} (L_{ij}^l - L_{ik}^l)^2 \\ &+ \sum_{l=0}^n \sum_{m>l}^n \frac{1}{(l+m+1)(l+m+3)(l+m+5)} \times (L_{ij}^l - L_{ik}^l)(L_{ij}^m - L_{ik}^m) \end{aligned} \quad (9)$$

Substituting Equations (8) and (9) into Equation (6), the similarity coefficients can be found. If n in Equation (9) is equal to 3, then the deviation sum of squares can be expressed. One can, for example, write expansion of $\eta(12,13)$ as follows:

$$\begin{aligned} \eta_1 = \eta(12, 13) &= \frac{1}{30} (L_{12}^0 - L_{13}^0)^2 + \frac{1}{210} (L_{12}^1 - L_{13}^1)^2 + \frac{1}{630} (L_{12}^2 - L_{13}^2)^2 \\ &+ \frac{1}{1386} (L_{12}^3 - L_{13}^3)^2 + \frac{1}{105} (L_{12}^0 - L_{13}^0)(L_{12}^2 - L_{13}^2) + \frac{1}{315} (L_{12}^1 - L_{13}^1)(L_{12}^3 - L_{13}^3) \end{aligned} \quad (10)$$

It is also possible to write some series expansions for the similarity coefficients values using Eq. (9).

2.2. Guggenheim's model

Guggenheim for the surface tension of a ternary solution can be expressed by the following equation:

$$e^{-(\gamma A/kT)} = e^{-(\gamma_1 A_1/kT)} + e^{-(\gamma_2 A_2/kT)} + e^{-(\gamma_3 A_3/kT)} \quad (11)$$

where γ is the surface tension of the ternary alloy, γ_i ($i = 1, 2$ and 3) is the surface tension of the components of the alloy, and A is the molar surface area of the alloy component which is defined by:

$$A_i = f' N_a^{(1/3)} V_i^{(2/3)} \quad (12)$$

where f' is the atomic arrangement factor for the liquid surface (1.09 for close packing and 1.12 for body centred cubic packing) and it can be possible to take $A_1=A_2=A_3=A$ (alloy). The expressions of density and atomic weight of the alloy can be written as

$$\rho(\text{alloy}) = \sum_{i=1}^3 X_i \rho_i \quad (13)$$

and

$$M(\text{alloy}) = \sum_{i=1}^3 X_i M_i \quad (14)$$

where ρ and ρ_i are the densities of liquid alloy and pure component i , respectively. M and M_i are atomic weights of the liquid alloy and components of the alloy i , respectively. The necessary condition of the calculation of A is to consider only the main component of the alloy which is mentioned above.

2.3. Egrý's model

A simple and important relationship between surface tension and viscosity has been established by Egrý et al. [46,47], which is given as

$$\frac{\gamma}{\eta} = \frac{15}{16} \sqrt{\frac{RT}{mN_a}} \quad (15)$$

Here, R , T and m are denoted as universal gas constant, absolute temperature and atomic mass. Using surface tension data, the surface tensions related with liquid Ni–Cu–Fe alloy were derived by Equation (15) using some models.

2.4. Muggianu's model

This model has a symmetrical property and its expression for the surface tension can be written as

$$\begin{aligned}\gamma^E &= \frac{4x_1x_2}{(1+x_1-x_2)(1+x_2-x_1)} \gamma_{12}^E \left(\frac{1+x_1-x_2}{2}; \frac{1+x_2-x_1}{2} \right) \\ &+ \frac{4x_1x_3}{(1+x_1-x_3)(1+x_3-x_1)} \gamma_{13}^E \left(\frac{1+x_1-x_3}{2}; \frac{1+x_3-x_1}{2} \right) \\ &+ \frac{4x_2x_3}{(1+x_2-x_3)(1+x_3-x_2)} \gamma_{23}^E \left(\frac{1+x_2-x_3}{2}; \frac{1+x_3-x_2}{2} \right)\end{aligned}\quad (16)$$

2.5. Kohler's model

This model has a symmetrical property and its expression for the surface tension can be written as:

$$\begin{aligned}\gamma^E &= (x_1+x_2)^2 \gamma_{12}^E \left(\frac{x_1}{x_1+x_2}; \frac{x_2}{x_1+x_2} \right) \\ &+ (x_1+x_3)^2 \gamma_{13}^E \left(\frac{x_1}{x_1+x_3}; \frac{x_3}{x_1+x_3} \right) \\ &+ (x_2+x_3)^2 \gamma_{23}^E \left(\frac{x_2}{x_2+x_3}; \frac{x_3}{x_2+x_3} \right)\end{aligned}\quad (17)$$

2.6. Toop's model

An expression of Toop's Model has an asymmetrical character and is given as

$$\begin{aligned}\gamma^E &= \frac{x_2}{1-x_1} \gamma_{12}^E(x_1; 1-x_1) + \frac{x_3}{1-x_1} \gamma_{13}^E(x_1; 1-x_1) \\ &+ (x_2+x_3)^2 \gamma_{23}^E \left(\frac{x_2}{x_2+x_3}; \frac{x_3}{x_2+x_3} \right)\end{aligned}\quad (18)$$

2.7. Hillert's model

An expression of Hillert's Model has an asymmetrical character and is given as

$$\begin{aligned}\gamma^E &= \frac{x_2x_3}{v_{23}v_{32}} \gamma_{23}^E(v_{23}; v_{32}) + \frac{x_2}{1+x_1} \gamma_{12}^E(x_1; 1-x_1) \\ &+ \frac{x_3}{1+x_1} \gamma_{13}^E(x_1; 1-x_1)\end{aligned}\quad (19)$$

where,

$$v_{ij} = \frac{1 + x_i - x_j}{2} \text{ and } v_{ji} = \frac{1 + x_j - x_i}{2} \quad (20)$$

2.8. Ideal solution model for quasi-binary system

A simple model for $\text{Cu}_x \text{Fe}_y \text{Ni}_{(1-y)}$ is given as follows ($0 < x < 1$ and $0 < y < 1$). In this model, the surface tension can be calculated from the ideal solution model. The average surface tension of a binary alloy $\text{Fe}_y \text{Ni}_{(1-y)}$ is given by the following expression:

$$\gamma_{\text{Fe-Ni}} = y\gamma_{\text{Fe}} + (1-y)\gamma_{\text{Ni}} \quad (21)$$

Using ideal solution model, the surface tension of a quasi-binary alloy system Cu-Me can be written as

$$\gamma_{\text{Cu-Me}} = x_{\text{Cu}}^S \gamma_{\text{Cu}} + (1 - x_{\text{Cu}}^S) \gamma_{\text{Fe-Ni}} \quad (22)$$

where Me is denoted as metal and x_{Cu}^S is the surface concentration and can be given as

$$x_{\text{Cu}}^S = x[x + (1-x)\exp^{(S_A(\gamma_{\text{Cu}} - \gamma_{\text{Fe-Ni}})/T)}]^{-1} \quad (23)$$

where the exponential term in this equation is known as surface segregation. Here, the expression for S_A is given as

$$S_A = \frac{(1.09N_a^{(1/3)}V_i^{(2/3)})}{R} \quad (24)$$

2.9. Butler's model

Butler's Model has been described in detail in numerous studies. However, some equations concerning with this model for ternary alloy system will be given shortly as follows: The surface tension of a mixture containing three components can be written as

$$\begin{aligned} \gamma &= \gamma_i + \frac{RT}{S_i} \ln\left(\frac{x_i^S}{x_i^B}\right) + \frac{1}{S_i} (\overline{\Delta G}_i^{E,S} - \overline{\Delta G}_i^{E,B}) \\ \gamma &= \gamma_j + \frac{RT}{S_j} \ln\left(\frac{x_j^S}{x_j^B}\right) + \frac{1}{S_j} (\overline{\Delta G}_j^{E,S} - \overline{\Delta G}_j^{E,B}) \\ \gamma &= \gamma_k + \frac{RT}{S_k} \ln\left(\frac{x_k^S}{x_k^B}\right) + \frac{1}{S_k} (\overline{\Delta G}_k^{E,S} - \overline{\Delta G}_k^{E,B}) \end{aligned} \quad (25)$$

where γ_i , γ_j and γ_k are the surface tensions of the pure components i th a mixing, S_i , S_j and S_k are the surface areas of components, and x_i^B , x_j^B and x_k^B and x_i^S , x_j^S and x_k^S are the mole fractions of components in the bulk and surface phases, respectively. An expression for surface area of one of components can be given in Guggenheim.

Since atoms in the surface layer have lower coordination numbers than in the bulk phase, it is clear that there is an assumption that the absolute value of partial excess Gibbs energy of a component in the surface layer of a liquid is smaller than that in the bulk phase. Therefore, the partial excess Gibbs energy of the i th component in the surface layer can be expressed as $G_i^{E, S} = \text{const } G_i^{E, B}$ [J / mol]. $\text{const} = z^S / z^B$. This constant is taken as 0.83 depending on the number of the nearest neighbours in the surface monolayer and bulk [53]. The expressions of the partial excess Gibbs energy, $G_i^{E, B}$, of the i th component of ternary systems in the bulk phase, as a function of T and x_i^B , are easily calculated.

4. Results and discussion

Although much information can be derived from thermodynamic predictions, it can be said that the actual experiment is still the most reliable method to determine the thermophysical properties of an investigated alloy systems. For this purpose, some researchers carefully followed the following procedures to prepare the samples. The surface tension measurements were performed using the oscillating drop technique in Ref. [34,54]. The alloy samples having corresponding Ni, Cu, and Fe concentrations were prepared by melting, together with the required amounts of the constituent elements in an arc furnace. Besides these processes, to remove any dissolve gas such as oxygen, each sample was shortly melted under vacuum conditions before the experimental measurements were performed. Then, the samples were melted in a levitation process to obtain a homogeneous alloy by the researchers in the Ref. [34].

Table 1 shows the measured parameters of the three elements Ni, Cu and Fe. These parameters are compared with corresponding values gathered from literature. The surface tension data obtained in our study have also been analysed in view of theoretical models. In addition to geometric and calphad models, GSM has become one of the most used models in recent years. In GSM model,

Table 1. Surface tension, melting temperatures and density of pure elements. Here, the temperature expressions of the surface tension and density of the pure elements are given as $\gamma_i(T) = \gamma_{m,i} + \gamma_{T,i}(T - T_{m,i})$ and $\rho_i(T) = \rho_{m,i} - \rho_{T,i}(T - T_{m,i})$ respectively.

Elements	Density		Melting temperature $T_{m,i}$ (K)	Ref.	Surface tension γ_i at 1800 K (mN/m)		Ref.
	$(10^{-6} \rho_{m,i} \text{ gr} / \text{cm}^3)$	$(10^{-4} \rho_{T,i} \text{ gr} / \text{cm}^3 \text{ K})$			Ref.	Ref.	
Ni	7.89	9.91	1728	[36]	1782	[55]	
Cu	8.033	7.953	1356	[36]	1224	[56]	
Fe	7.035	9.26	1811	[36]	1915	[55]	

deviation sum of square and similarity coefficients should be calculated before starting to calculate the surface tension values. The values of the mentioned parameters are determined as $\eta_1 = \eta(12,13) = 0.006996$, $\eta_2 = \eta(21,23) = 0.03767$ and $\eta_3 = \eta(31,32) = 0.07694$, $\xi_{12} = 0.15665$, $\xi_{23} = 0.328653$ and $\xi_{31} = 0.91665$, respectively. In order to calculate these parameters, the coefficients of Redlich–Kister–Muggianu polynomial are determined from the excess surface tension experiments in the present work:

$$\gamma^E \left(\frac{mN}{m} \right) = X_i X_j \sum_{k=0}^n A_{ij}^k (X_i X_j)^k \quad (26)$$

The parameters are as called A_{12}^0 , A_{12}^1 and A_{12}^2 . The extremum values of excess surface tension for each of binary mixtures are shown in Table 2 along with the standard deviations $\sigma(\gamma^E)$. The standard deviations are calculated using Equation (27):

$$\sigma(\gamma^E) = [(\gamma_{\text{obs}}^E - \gamma_{\text{cal}}^E)^2 / (X_{\text{obs}} - n)]^{1/2} \quad (27)$$

where n is the number of polynomial coefficients.

The excess surface tensions of the mixtures just mentioned above at 1800K for the concentrations of the considered samples along with Section A: $\text{Ni}_{0.4(1-x)}\text{Cu}_x\text{Fe}_{0.6(1-x)}$ and Section B: $(\text{Ni}_x\text{Cu}_{0.2}\text{Fe}_{0.8-x})$ [34] in Figure 1 are plotted against the mole fraction of second components in Figures 1–3. In these figures, the values of excess surface tensions show a sigmoid kind of behaviour for the binary mixtures Ni–Cu, Ni–Fe and Cu–Fe. It can be seen that the changes in the excess surface tensions of the binary mixtures are negative throughout the entire composition range of second components. It is clearly seen from Figure 2 that a relatively deep minimum of excess surface tension of Fe–Cu alloys with respect to other two alloy systems is associated with great positive interaction energy that indicates a strong tendency to demixing. It is better to pick up Fe as the asymmetric component for Toop’s Model, since the Ni–Fe and Cu–Fe two binary systems are much more similar thermodynamically, shown in Figure 2. On the other hand, it is seen from GSM model that the calculated similarity coefficient in this study is $\xi_{12} = 0.917$ and it means that Cu is relatively similar to Ni, indicating that we have no alternative option but to select Fe as the asymmetric component. According to this case, it can be seen that the

Table 2. Calculated Redlich–Kister parameters concerning the surface tension of the binary liquid alloys, Ni–Cu, Cu–Fe and Fe–Ni along with their standard deviation.

Alloy systems	A_{12}^0	A_{12}^1	A_{12}^2	Standard deviation
Ni–Cu	–0.3087	–0.2817	0.3013	0.0177
Cu–Fe	–1.0421	0.9885	–2.0729	0.0231
Fe–Ni	0.1027	0.0236	–0.0603	0.0175

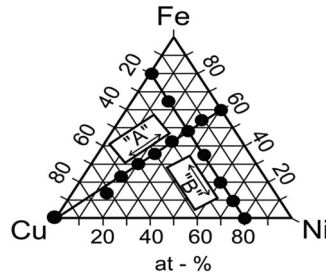


Figure 1. Concentrations of the considered samples along with Section A: $Ni_{0.4(1-x)}Cu_xFe_{0.6(1-x)}$ and Section B: $(Ni_xCu_{0.2}Fe_{0.8-x})$. This figure is taken from the Ref. [34].

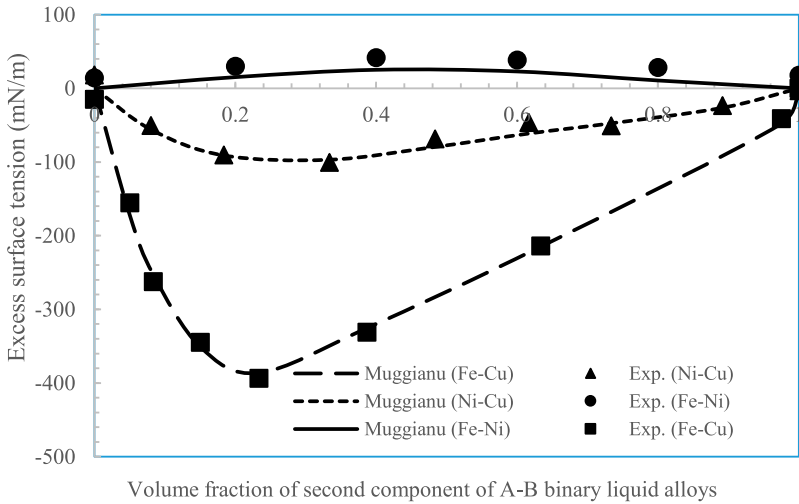


Figure 2. The calculated excess surface tensions associated with Ni–Cu, Ni–Fe and Cu–Fe binary liquid alloys along with their experimental values [57,58].

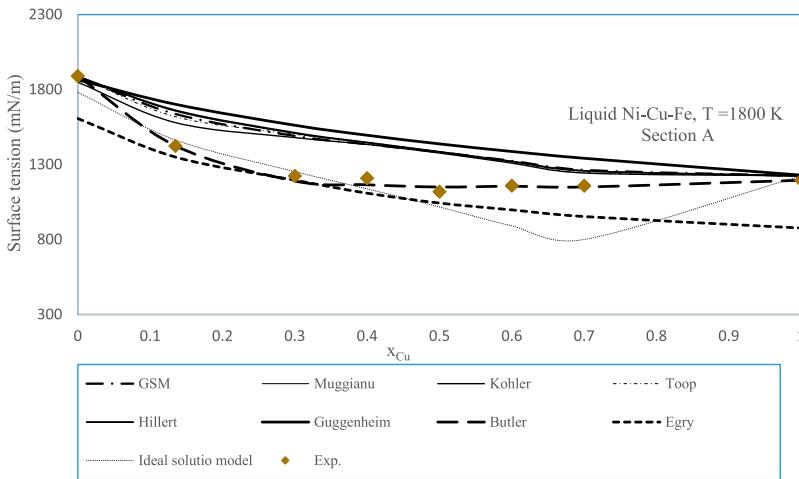


Figure 3. The calculated surface tension and experimental values of Ni–Cu–Fe liquid alloy systems in Section A at $T = 1800K$ versus copper concentration

Ni–Cu–Fe ternary system is not exactly Kohler’s Model nor Toop’s Model so that both the Kohler’s Model and the Toop’s Model cannot obtain accurate predicted values [43,59]. It was proved that GSM model is a general geometric model and that all traditional geometric models used in this study, such as the Muggianu’s model, Kohler’s Model, Hillert’s Model and Toop’s Model, are special sub-forms of the general geometric models that provide different situations. Therefore, in this study, the predicted surface tension curves calculated by the GSM model should be recommended along with those calculated from the other traditional models. In the present work, for the fluid alloy Ni–Cu–Fe, we make a comparison between the results obtained from the models described in the introduction and the newly measured experimental data [34].

The surface tensions, γ , were calculated at 1800 K for each concentration x_{Cu} and x_{Ni} in Sections A and B, respectively. The results are also shown in Figures 3 and 4. The experimental surface tension values in Section A decreases from 1880 (mN/m) down to 1500 (mN/m) as the Cu content is increased up to nearly 0.13 while the surface tension for higher Cu content, remains almost constant between the levels 1200 and 1300 (mN/m). It is seen from Table 1 that this value corresponds nearly to the value of pure Cu. All experimental values of the surface tension in Section B are in a range between 1300 (mN/m) up to 1450 (mN/m) and nearly constant. The graphs obtained from surface tension calculations using all models, except for Butler’s Model, give very close values to each other mutually. Moreover, the graphs in this study become difficult to distinguish between one another due to the overlap of the graphs plotted for the models. Therefore, the root mean square deviation, S, analysis was carried out for the data of the ternary systems. An expression for this can be written as

$$S = \left(\frac{1}{N} \right) \left\{ \sum_{i=1}^N (\sigma_{exp,i}^E - \sigma_{cal,i}^E)^2 \right\}^{1/2} \quad (28)$$

Instead of examining curves mentioned above, the statistical analysis was performed for each model. For this reason, the reproducibility is evaluated by way of

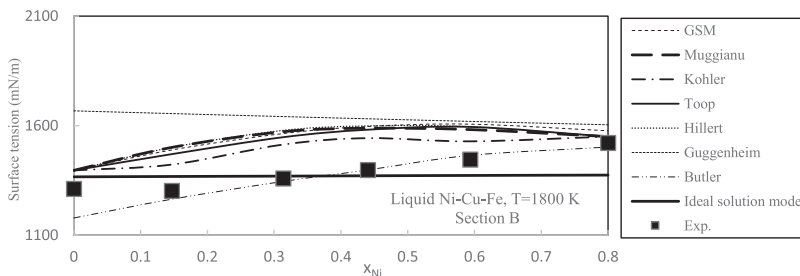


Figure 4. The calculated surface tension and experimental values of Ni –Cu–Fe liquid alloy systems in Section B at $T = 1800\text{K}$ versus nickel concentration.

the root mean square deviation values, S , of the surface tension of Ni–Cu–Fe liquid alloy systems in which they are also calculated for Sections A and B at 1800 K. The obtained results are given in Table 3. It is concluded that due to S -values of 8.17 and 23.7 for Sections A and B respectively, the Butler’s Model among all models seems to be the best model to represent the experimental data in the present ternary alloy system. The surface tension values in Section A decreases from 1880 (mN/m) down to 1500 (mN/m) as the Cu content is increased up to nearly 0.13, in which this situation concerning all model treated in this work has also an agreement for Cu content. GSM, Guggenheim’s Model and geometrical models for Section A are in agreement mutually. The surface tension values obtained from these models are considerably larger than those of the Egry’s and Butler’s Models (the values of these models and experiment results [34, 35] are in good agreement one another in the range $0.1 < x_{\text{Cu}} < 0.5$). The description on the ideal solution model is given in the next paragraph. GSM and geometrical models for Section B are in agreement mutually and it is found that the surface tension values of these models for $x_{\text{Cu}} > 0.5$ are close to the results of the experimental values. The surface tension values obtained from Butler’s Model are quite different from the results of the experimental values in the range $0 < x_{\text{Cu}} < 0.1$. The description on the ideal solution model is also given in the next paragraph. In addition, it is seen from the Section B that the values of the surface tension are nearly in a range between 1200 and 1680 (mN/m) for models treated in this study. The observed increase in the surface tension is very small, as the concentration Ni increases. This case can be justified to consider the surface tension as a constant in section B. Although all theoretical models give an approximate result to experimental values, it is clear from Table 3 that the mean square deviation is the smallest obtained value for Butler’s Model. The values obtained with the ideal solution model are close to the Butler’s Model, but the Butler’s Model appears to be the best model representing the experimental data in both Sections A and B in this alloy system. The concentration dependence of the surface tension ideal solution and Butler’s Model show nonlinear behaviour for Section A of Ni–Cu–Fe alloys except for other models displaying nearly linear character. This phenomenon has also been observed in ideal solution, Guggenheim’s Model and Butler’s Model for Section B of Ni–Cu–Fe alloys except for other models displaying nearly linear character. These behaviours have also been observed for the binary liquid alloys Cu–Ni by Gorges [25,60], Cu–Fe

Table 3. The root mean square deviation values of the surface tension of Ni–Cu–Fe liquid alloy systems calculated for Sections A and B at 1800K.

Section	GSM	Muggianu	Kohler	Toop	Hillert	Guggenheim	Butler	Egry	Ideal solution
A	65.4	67.9	51.6	56.4	60.0	84.6	8.17	65.5	25.4
B	65.0	64.0	45.3	59.4	66.2	108.2	23.70		–28.2

[25,29,61] and Ni-Fe [25,61]. It is concluded that such a behaviour mentioned above can be explained by a subregular solution model.

According to the authors in this study, the Butler's Model uses the values of the pure elements in the calculation of the surface tension values of the alloy. Therefore, the values of this model are closer to experimental results. As the number of parameters used in other models increase, obtained values differ slightly from experimental results.

It is seen from Figure 5 that the curves of Egry and Kaptay [62] at melting temperature of Ni-Cu-Fe for Section A yield different slopes for $\alpha_{\eta-\gamma}$, i.e. 0.94 and 0.75; while in this study, the slope in question is calculated as 0.9325. It is obviously seen that there is tendency in Figure 5, that the ratio (Surface tension /viscosity) associated with Ni-Cu-Fe liquid alloy systems for Section A increases linearly as the expression $(RT_m/M)^{1/2}$ increases. The experimental values of surface tensions calculated using Guggenheim's Model for liquid Ni-Cu-Fe samples and temperature (Section A) are compared in Figure 6. It is seen obviously that the values of the surface tensions decrease with the increase of the Cu content and there is a parallelism in slopes of the data line between experimental and theoretical surface tension values.

On the other hand, the segregation factor S_0 determined in ideal solution model mentioned in Introduction is given by:

$$S_0 = \exp \frac{S_A(\gamma_{Cu} - \gamma_{FeNi})}{T} \quad (29)$$

where the surface tension γ_{FeNi} for a binary alloy is exchanged with another metal's surface tension in the binary alloys. This case is investigated for the surface tension associated with some binary liquid alloys treated by the authors in this study [1,13]. On the other hand, it should be emphasised that

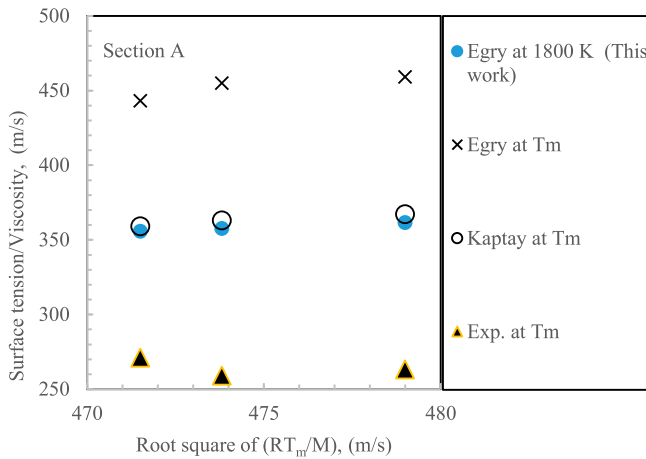


Figure 5. Ratio (Surface tension /viscosity) associated with Ni-Cu-Fe liquid alloy systems for Section A at $T = 1800\text{K}$ versus $(RT_m/M)^{1/2}$.

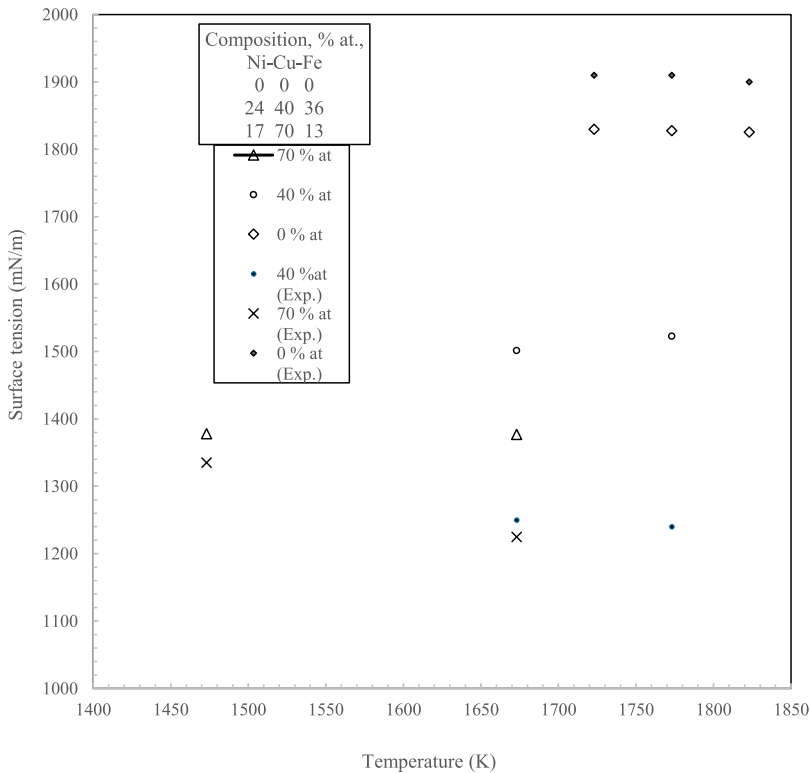


Figure 6. Comparison of the experimental surface tension values with those of calculated from Guggenheim's Model for liquid Ni-Cu-Fe samples as a function of temperature (Section A).

surface segregation is an important key factor in determining surface tension of an alloy. The component with the lowest surface tension in an alloy, is reported by Egry [63,64], which tends to dissociate at the surface in order to reduce the total energy of the system. It is well known that the surface separation leads to a concave shape of the surface tension as a function of the concentration, i.e. lowering the surface tension below the linear interpolation between the two components. This is evident from Figure 3, for the quasi-binary Cu-Me system. As can also be seen from Figure 3 that a distinctive Cu separation occurs in the surface layer.

The ideal solution model in the original form [35], does not have fitting parameters, and only contains the temperature, surface tensions of the three pure components and concentrations of the bulk phase to calculate the surface tension and surface composition quantities. It is well known that the surface segregation values in the ideal solution model are estimated as small values. If applied in this condition, the segregation factor will cause erroneous results in the small values of the concentration. In order to compensate for this effect, the S_A fitting parameter of the ideal solution model in the original form is increased by 50% artificially and the value $S_A = 6000 \text{ K m/N}$ (for transition

metals approximately $S_A = 4000 \text{ Km / N}$) is taken as constant in calculations of the surface tension and surface composition. As a result of this adjustment, the surface tension values of the Cu-Fe-Ni system were found to be much closer to the experimental results. The value of the fitting parameter depends on the molar volume of the alloy and the Avogadro's number (also the value of molar volume depends on the temperature of the alloy). In order to accurately reflect the effect of the molar volume of the alloy in the related equations, the value of S_A in this study is taken as 4219, 4528 and 4510 Km/N for Ni, Cu and Fe, respectively. Therefore, surface tension values were found to be quite small from the experimental results for along sections A and B of the ternary alloy system.

5. Conclusions

The applicability of the models mentioned above to the alloys is tested by means of two sections of the liquid alloys Ni-Cu-Fe. These liquid systems are selected from the literature because reliable surface tension data exist for both sections. Using different models, the surface tension can be derived from the knowledge, such as the surface tension, molar volume and melting temperatures of the components concerning unary and binary phases; without further knowledge about the ternary system. Some important results are summarised as follows: The excess surface tensions of the binary liquid alloys Ni-Cu, Fe-Ni and Cu-Fe are negative throughout the entire composition range of second components. It is found that Fe component is the asymmetric component for Toop's Model from the investigation of the excess surface tensions of the binary liquid alloys mentioned above. It is concluded from the root mean square deviation values that due to S-values of 8.17 and 23.7 for Section A and B respectively, Butler's Model among all models seems to be the best model to represent the experimental data in the present liquid ternary alloy system Ni-Cu-Fe.

Disclosure statement

No potential conflict of interest was reported by the authors.

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