Temperature dependences of surface tension, density and viscosity study of Sn-Ag-Cu with Bi additions using theoretical models

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In this work, the kohler, Muggianu,Toop and Hillert geometric models were used to calculate the surface tension, molar volume and density of the liquid Sn-Ag-Cu-Bi quaternary alloys along three selected sections $x_{\text{Sn}}:x_{\text{Ag}}:x_{\text{Cu}} = 1:1:1, 1:1:2$ and $1:2:1$ in the temperature range of 923 K–1423 K. The choice of this temperature range was made on the basis of the calculation results of the liquidus line of the alloys belonging to the three sections. The same properties have been estimated for five selected Sn$_{2.7}$Ag$_{0.86}$Cu$_{3.86}$Bi, Sn$_{3.13}$Ag$_{0.48}$Cu$_{4.02}$Bi, Sn$_{2.95}$Ag$_{0.53}$Cu$_{6.81}$Bi, Sn$_{2.68}$Ag$_{1.01}$Cu$_{6.62}$Bi and Sn$_{3.24}$Ag$_{0.75}$Cu$_{1.76}$Bi quaternary alloys between 623 K and 1123 K for comparison with the available experimental data. Moreover, the surface tension and density of these five alloys have also been calculated on the basis of Guggenheim and theoretical equation, respectively. In addition, the Seetharaman-sichen and Kaptay equations were extended to estimate the viscosity of SAC + Bi alloys.

We also discussed the influence of Bismuth addition in liquid Sn-Ag-Cu-Bi. Estimated values show that Bi increases molar volume and density but decreases the surface tension and viscosity. On the other hand, the surface tensions diminish with the temperature for the all studied models, with the exception of some concentration of Bismuth; an inverse tendency is observed $(d\sigma/dT)>0$. While, the density diminishes with increasing temperature for all alloys $(d\sigma/dT)<0$. These models have been shown to be a great alternative for calculating the thermo-physical properties of quaternary systems.

In recent years, researchers have been very interested in identifying alternatives for lead solders because they are harmful to the environment. This trend has been encouraged in Europe by the RoHS and WEEE European Directive. Based on the analysis of several multi-component systems, two sets of alloys are potential substitutes for lead soldering. The first groups are the Sn-Ag-Cu (SAC) alloys with the addition of different metals (Bi, Zn, In and Sb)\textsuperscript{1–6}. Previous studies have recommended the Sn-Ag-Cu-Bi quaternary system as a promising candidate for lead-free solders, as the biggest advantage of SnAgCuBi over welds SnAgCu is the lower melting temperature. In SnAgCuBi, bismuth plays an important role in lowering the melting temperature of the alloy. It is possible to reduce the melting temperature of the alloy from 217 $^\circ$C to 208 $^\circ$C, by balancing the amount of bismuth as well as the amounts of silver and copper in the alloys. However, the addition of Bi to Sn-Ag-Cu alloys increases the mechanical properties of solders\textsuperscript{7}.

Since surface properties play a key role in the development of welding, the development of new welds requires data on thermophysical properties such as surface tension that can be obtained experimentally or by numerical modeling if reliable data exist for subsystems and pure components. In addition, theoretical model is sometimes preferred because of the increasing complexity and costs of experimentation, especially for multi-component systems (quaternary, quinary...). The analysis of the influence of the amount of bismuth in the Sn-Ag-Cu-Bi quaternary welds on various properties was carried out by Hwang\textsuperscript{8} and Takao et al.\textsuperscript{9}. However, little previous work on thermo-physical and electrical properties has been reported in the literature\textsuperscript{10}. Indeed, Moser et al.\textsuperscript{11}, in 2006, have measured the thermo-physical and mechanical proprieties of Sn-Ag-Cu- eutectic alloy with different additions of Bismuth using different techniques. They showed a linear dependence of surface tension as a function of
temperature. At the same time, Ohnuma et al.11 have studied the surface tension of Sn-Ag-Cu-Bi liquid alloys using Butler equation13. Their results have been compared with some experimental values11. Later, Ganczarz et al.14 have measured the surface tension, density and viscosity of Sn2.92 Ag0.4Cu3.07 Bi liquid alloy as a function of temperature by using different methods. The obtained results showed that the addition of Bi to the SAC increases the density and decreases the surface tension and the viscosity. In addition, they showed that the properties studied by different methods (maximum bubble pressure, dilatometry, capillary flow and discharge crucible) were almost similar.

In the present paper, we presented the theoretical results of the surface tension, molar volume and density of Sn-Ag-Cu-Bi system using different geometric models, Kohler15, Muggianu16, Toop17 and Hillert18. The geometric models are used in this work in order to verify their effectiveness since they are considered as the most widespread theoretical models used for metallic alloys, especially for ternary systems. As well as, surface tension and density predicted by the Guggenheim19 and theoretical equations20, respectively. In addition, we presented the theoretical models used for metallic alloys, especially for ternary systems. As well as, surface tension and density predicted by the Seetharaman-Sichen21 and Kaptay equations22 and the predicted results are compared to each other and to the experimental ones11,14.

Our calculations were done along three cross-sections $x_{Sn}$:$x_{Ag}$:$x_{Cu}$ = 1:1:1, 1:1:2 and 1:2:1 between 923 K and 1423 K and Sn2.7Ag0.86Cu3.86Bi, Sn3.13Ag0.48Cu4.02Bi, Sn2.95Ag0.53Cu4.02Bi, Sn2.68Ag1.01Cu6.62Bi and Sn3.24 Ag0.75 Cu1.76 Bi quaternary alloys in the temperature range 623 K–1123 K.

**Method of Calculation**

Numerous studies have been carried out for the creation of adequate databases of thermo-physical properties (surface tension, density and viscosity) of Sn, Ag, Cu and Bi under the framework of developing lead-free solders. In this work, we used the pure constituents of Sn, Ag, Cu and Bi inside the temperature range (523 K–1473 K) of our prediction. Moreover, among these numerous studies, we have chosen the values for pure elements that led to values of quaternary system Sn-Ag-Cu-Bi closest to the experimental ones.

**Modeling surface tension of liquid Sn-Ag-Cu-Bi system from geometric models.** The information of the properties of binary alloys is indispensable for the prediction of thermo-physical properties of quaternary alloys for the purpose of comparing with experimental data. The models proposed by various researchers are exposed in the following sections. The models of Kohler15 and Muggianu et al.16 were used in this work as simple models based on binary data, while the Toop17 and Hillert18 models are asymmetric.

**Kohler model.** The Kohler and Muggianu models have been used to estimate the surface tension of Sn-Ag-Cu-Bi quaternary alloys. Consequently, the properties of any quaternary system can be calculated from the knowledge of the corresponding properties of the boundary binaries.

Indeed, for the two symmetric models, the surface tension for a four-component system has been expressed by the following equations:

$$\sigma^{E}_{1-2-3-4} = (x_1 + x_3)^2 \cdot \sigma^{E}_{12} \left( \frac{x_1}{x_1 + x_2}, \frac{x_3}{x_1 + x_3} \right) + (x_1 + x_4)^2 \cdot \sigma^{E}_{14} \left( \frac{x_1}{x_1 + x_2}, \frac{x_4}{x_1 + x_4} \right) + (x_2 + x_4)^2 \cdot \sigma^{E}_{24} \left( \frac{x_2}{x_2 + x_3}, \frac{x_4}{x_2 + x_4} \right) + (x_3 + x_4)^2 \cdot \sigma^{E}_{34} \left( \frac{x_3}{x_3 + x_4}, \frac{x_4}{x_3 + x_4} \right)$$

$$\sigma^{E}_{12-3-4} = (x_1 + x_3)^2 \cdot \sigma^{E}_{13} \left( \frac{1}{1 + x_1 - x_3}, \frac{1}{1 + x_2 - x_3} \right) + (x_1 + x_4)^2 \cdot \sigma^{E}_{14} \left( \frac{1}{1 + x_1 - x_4}, \frac{1}{1 + x_2 - x_4} \right) + (x_2 + x_4)^2 \cdot \sigma^{E}_{24} \left( \frac{1}{1 + x_2 - x_4}, \frac{1}{1 + x_3 - x_4} \right) + (x_3 + x_4)^2 \cdot \sigma^{E}_{34} \left( \frac{1}{1 + x_3 - x_4}, \frac{1}{1 + x_4 - x_4} \right)$$

**Muggianu model.**

$$\sigma^{E}_{1-2-3-4} = \frac{4x_1 x_2}{(1 + x_1 - x_2)(1 + x_2 - x_1)} \cdot \sigma^{E}_{12} \left( 1 + x_1 - x_2, \frac{1}{2} \right) + \frac{4x_1 x_3}{(1 + x_1 - x_3)(1 + x_3 - x_1)} \cdot \sigma^{E}_{13} \left( 1 + x_1 - x_3, \frac{1}{2} \right) + \frac{4x_2 x_3}{(1 + x_2 - x_3)(1 + x_3 - x_2)} \cdot \sigma^{E}_{23} \left( 1 + x_2 - x_3, \frac{1}{2} \right) + \frac{4x_1 x_4}{(1 + x_1 - x_4)(1 + x_4 - x_1)} \cdot \sigma^{E}_{14} \left( 1 + x_1 - x_4, \frac{1}{2} \right) + \frac{4x_2 x_4}{(1 + x_2 - x_4)(1 + x_4 - x_2)} \cdot \sigma^{E}_{24} \left( 1 + x_2 - x_4, \frac{1}{2} \right) + \frac{4x_3 x_4}{(1 + x_3 - x_4)(1 + x_4 - x_3)} \cdot \sigma^{E}_{34} \left( 1 + x_3 - x_4, \frac{1}{2} \right)$$

**Toop model.** On the other hand, the asymmetric models of Toop and Hillert are respectively expressed by the two equations:
The excess surface tension of six binary systems. The excess surface tension $\sigma^E$ for binary system is a composition dependency of surface tension of mixture that can be defined as follows:

$$\sigma^E = \sigma - \sigma^I$$  \hspace{1cm} (5)

with $\sigma$ and $\sigma^I$ represent the surface tension of binary alloys and the surface tension of the ideal alloys, respectively. $\sigma^I$ can be defined as following:

$$\sigma^I = X_i \sigma_{i} + X_j \sigma_{j}$$  \hspace{1cm} (6)

with $X_i$ and $\sigma_i$ represent the molar fraction of a constituent $i$ and the surface tension of the pure constituent $i$, respectively. The surface tension, as a function of temperature, of the pure constituent $i$ is presented in Table 1.

The excess surface tension values of the six binary alloys are taken from previous work Sn-Ag\(^{23}\), Sn-Cu\(^{24}\), Sn-Bi\(^{23}\), Ag-Cu\(^{25}\) and Ag-Bi\(^{23}\). The values of Cu-Bi sub-binary alloys are predicted based on Butler's equation\(^{13}\).

Using of guggenheim equation. Based on the model of regular solutions, the Guggenheim\(^{19}\) equation relies on statistical approximations, in which the constituents of the binary are distributed randomly within the quasi-crystalline liquid. Moreover, this equation has been developed for quaternary alloys, which can be written in the form:

$$\exp \left( - \frac{\sigma_1 A}{RT} \right) = x_1 \exp \left( - \frac{\sigma_{A_1}}{RT} \right) + x_2 \exp \left( - \frac{\sigma_{A_2}}{RT} \right) + x_3 \exp \left( - \frac{\sigma_{A_3}}{RT} \right) + x_4 \exp \left( - \frac{\sigma_{A_4}}{RT} \right)$$  \hspace{1cm} (7)

where $\sigma_3$ is the surface tension of the ternary system, $\sigma_{A_1}$, $\sigma_{A_2}$, $\sigma_{A_3}$ and $\sigma_{A_4}$ are surface tensions of the individual components of the alloy, and $A$ is the molar surface area which is defined by:

$$A = \rho \frac{N_A}{M} M^{2/3}$$  \hspace{1cm} (8)

$\rho = \sum x_i \rho_i$ and $M = \sum x_i M_i$.

$\rho$ and $\rho_i$ represent the densities of quaternary alloys and pure constituent $i$, respectively. $M$ and $M_i$ are atomic weights of the quaternary alloys and pure constituent $i$, respectively (Table 2). $N_A$ is the Avogadro number and $f$ is the atomic arrangement factor for the liquid surface.

### Table 1. Surface tension of the pure constituents.

| Constituents | $\sigma_1$ (mN/m) | Reference |
|--------------|------------------|-----------|
| Sn           | 636.5–0.1101 T   |            |
| Ag           | 1164–0.204 T     |            |
| Cu           | 1475.648–0.14224 T |          |
| Bi           | 431–0.08 T       |            |
The excess molar volume of six binary systems. In this research, we used Kohler\textsuperscript{15}, Muggianu\textsuperscript{16}, Toop\textsuperscript{17} and Hillert\textsuperscript{18} to calculate molar volume of Sn-Ag-Cu-Bi alloys. The excess molar volume, $V^E$, for binary system is a composition dependency of molar volume of mixture that can be defined as follows:

$$V^E = V - V^i$$

(9)

$V$ and $V^i$ represent the molar volume of binary alloys and the molar volume of the ideal alloys, respectively. $V^i$ can be defined as follow:

$$V^i = X_1V_1 + X_2V_2$$

(10)

where $X_i$ and $V_i$ represent the molar fraction of a constituent $i$ and the molar volume of the pure constituent $i$, respectively (Table 3).

The excess molar volume values of the sub-binary systems are taken from previous work Sn-Ag\textsuperscript{23}, Sn-Cu\textsuperscript{24}, Sn-Bi\textsuperscript{23}, Ag-Cu\textsuperscript{25} and Ag-Bi\textsuperscript{23}.

The molar volume of Cu-Bi binary system was estimated using:

$$V_M = \frac{\sum x_i M_i}{\rho}$$

(11)

$\rho$ represents the density of binary Cu-Bi alloys, $x_i$ and $M_i$ are the molar fraction and molar mass of constituent $i$, respectively.

Calculation of molar volume of liquid phase in the Sn-Ag-Cu-Bi system. The same equations previously used for the calculation of the excess surface tension $\sigma^E$ will be used for the calculation of the excess molar volume $V^E$.

Density calculation of liquid the Sn-Ag-Cu-Bi system. The relationship between density and molar volume is an example is expressed as:

$$\rho = \frac{\sum x_i M_i}{V_M}$$

(12)

where $\rho$ is the density of mixture, while $x_i$ and $M_i$ are the molar fraction and molar mass of component $i$. $V_M$ is a molar volume of a mixture, calculated using Kohler\textsuperscript{15}, Muggianu\textsuperscript{16}, Toop\textsuperscript{17} and Hillert\textsuperscript{18} models.

The mathematical prediction of density is based on semi-empirical equations as well as on theoretical equations\textsuperscript{20}, ever since the atomic volumes of most liquid binary alloys is in fact a linear equation of composition, the calculation of alloy density can be approximated by an addition. A similar procedure can be used for higher order alloys, as indicated by:

$$\rho = x_1 \rho_1 + x_2 \rho_2 + x_3 \rho_3 + x_4 \rho_4$$

(13)

where $x_1, x_2, x_3, x_4$ are the atomic fractions of the constituents of the alloys, $\rho_1, \rho_2, \rho_3$ and $\rho_4$ are the densities of the pure components (Table 2).

Viscosity in the liquid Sn-Ag-Cu-Sn quaternary alloys. Viscosity is one of the key properties of alloys that influence the performance of pyrometallurgical processes in several ways. As such, the researcher has made considerable efforts in numerous experimental studies to quantify the dependence on viscosity composition and temperature of many simple and complex alloy systems. However, because of the problems and difficulties inherent in high temperature measurements, the available experimental results only cover a limited range of compositions and temperatures and do not fully meet the needs of the industry. In addition, the accuracy or reliability

| Constituents | $\rho$(g/cm$^3$) | $M_i$(g/mol) | Reference |
|-------------|----------------|-------------|-----------|
| Sn          | 7.118–0.00051 T | 118.6900    |          |
| Ag          | 10.18–0.00071 T | 107.8680    |          |
| Cu          | 9.485–0.001 T   | 63.546      |          |
| Bi          | 10.73–0.0012 T  | 208.9804    |          |

Table 2. Data on density and atomic mass of the pure constituents

| Constituents | $V_i$(m$^3$/mol) | Reference |
|-------------|-----------------|-----------|
| Sn          | 17.0.10$^{-4}$(1.0 + 0.000087(T-504.99)) |          |
| Ag          | 11.6.10$^{-4}$(1.0 + 0.000098(T-1234)) |          |
| Cu          | 7.94. 10$^{-6}$(1.0 + 0.000011(T-1357.77)) |          |
| Bi          | 20.80.10$^{-4}$(1.0 + 0.000117(T-544.1)) |          |

Table 3. Molar volume of the pure constituents.
of some published data has been found to be unsatisfactory. The discrepancy between some of the data is significantly large26.

As a result, in recent decades, various models have been allocated to calculate the viscosity of metal alloys. These models are based on one of the theoretical equations used to estimate the viscosity of single liquids, such as Eyring’s equation27, the Bockris Bockris’ equation28, Weymann’s equation29 and Frenkel’s equation30. There have also been some studies to correlate viscosity with self-defined parameters to find some consistency26. All modeling and correlation studies were useful and provided a reasonably good description of viscosity over a range of temperatures and compositions.

Seetharaman-Sichen equation. The Seetharaman-Du Sichen equation21 is a mathematical equation for estimation the viscosity used and developed for quaternary Sn-Ag-Cu-Bi alloys:

\[
\eta = \frac{hN_A\rho}{M} \exp \left( \frac{\Delta G^*}{RT} \right)
\]

where \( \rho \) and \( \rho_i \) are the density of liquid alloys and pure component \( i \), respectively. \( M \) and \( M_i \) are atomic weights of the liquid alloy and pure component \( i \), respectively, \( h \) is Planck’s constant. \( N_A \) is Avogadro’s number. \( \Delta G^* \) represents the Gibbs activation energy for viscosity. We can express this energy in the form:

\[
\Delta G^* = \sum x_i \Delta G_i^* + 3RT \sum x_i x_j + 3RT \sum x_i \ln x_i + \Delta G_{1-2-3-4}^E(T, \rho_0)
\]

where \( \Delta G_i^* \) is the Gibbs activation energy of the viscous flow in pure constituent \( i \)

\[
\Delta G_i^* = RT \ln \left( \frac{\eta_i M_i}{hN_A \rho_i} \right)
\]

\( \eta_i \) is the viscosity of the pure constituent \( i \) (Pa.s) (Table 4) and \( R = 8.314 \text{ J.mol}^{-1}\text{K}^{-1} \) and \( \Delta G_{1-2-3-4}^E(T, \rho_0) \) is the excess energy of alloy in the liquid phase for quaternary alloys.

This excess Gibbs energy was calculated using the Kohler geometric15.

\[
\Delta G_{1-2-3-4}^E = (x_1 + x_2)^2 \cdot \Delta G_{12}^E \left( \frac{x_1}{x_1 + x_2}, \frac{x_2}{x_1 + x_2} \right) + (x_1 + x_3)^2 \cdot \Delta G_{13}^E \left( \frac{x_1}{x_1 + x_3}, \frac{x_3}{x_1 + x_3} \right) + (x_1 + x_4)^2 \cdot \Delta G_{14}^E \left( \frac{x_1}{x_1 + x_4}, \frac{x_4}{x_1 + x_4} \right) + (x_2 + x_3)^2 \cdot \Delta G_{23}^E \left( \frac{x_2}{x_2 + x_3}, \frac{x_3}{x_2 + x_3} \right) + (x_2 + x_4)^2 \cdot \Delta G_{24}^E \left( \frac{x_2}{x_2 + x_4}, \frac{x_4}{x_2 + x_4} \right) + (x_3 + x_4)^2 \cdot \Delta G_{34}^E \left( \frac{x_3}{x_3 + x_4}, \frac{x_4}{x_3 + x_4} \right)
\]

\( \Delta G_{12}^E, \Delta G_{13}^E, \Delta G_{14}^E, \Delta G_{23}^E, \Delta G_{24}^E \) and \( \Delta G_{34}^E \) represent the excess Gibbs energies of the boundary binary systems taken along the quasi-binary sections \( X_i/X_i = x_i/x_i, x_i \) and \( X_i \) are respectively the molar fraction of a constituent \( i \) in the quaternary system and binary system.

The contribution of the six binary systems for the Sn-Ag-Cu-Bi quaternary alloy is described by polynomial Redlich-Kister polynomial31:

| Constituents | \( \eta_i(\text{mPa.s}) \) | Reference |
|--------------|-----------------|----------|
| Sn           | 0.4475Exp\((\frac{61914}{RT})\) | 41       |
| Ag           | 0.5976Exp\((\frac{19136}{RT})\) | 37       |
| Cu           | 1.769Exp\((\frac{10833}{RT})\) | 43       |
| Bi           | 0.445Exp\((\frac{6450}{RT})\) | 38       |

Table 4. Data on viscosity of the pure constituents.
Figure 1. Calculated phase diagrams for the Sn-Ag-Cu-Bi along three selected sections of $x_{\text{Sn}}:x_{\text{Ag}}:x_{\text{Cu}} = 1:1:1$, 1:1:2 and 1:2:1.

$$\Delta G_1^E = x_{\text{Sn}}^2(L_{12}^0 + L_{13}^1(X_1 - X_3) + L_{14}^2(X_1 - X_4)^2)$$
$$\Delta G_2^E = x_{\text{Sn}}x_{\text{Ag}}(L_{13}^0 + L_{13}^1(X_1 - X_3) + L_{14}^2(X_1 - X_4)^2)$$
$$\Delta G_3^E = x_{\text{Sn}}x_{\text{Cu}}(L_{14}^0 + L_{14}^1(X_1 - X_4) + L_{14}^2(X_1 - X_4)^2)$$
$$\Delta G_23^E = x_{\text{Ag}}x_{\text{Cu}}(L_{23}^0 + L_{23}^1(X_2 - X_3) + L_{24}^2(X_2 - X_4)^2)$$
$$\Delta G_24^E = x_{\text{Ag}}x_{\text{Cu}}(L_{24}^0 + L_{24}^1(X_2 - X_4) + L_{24}^2(X_2 - X_4)^2)$$
$$\Delta G_34^E = x_{\text{Ag}}x_{\text{In}}(L_{34}^0 + L_{34}^1(X_3 - X_4) + L_{34}^2(X_3 - X_4)^2)$$

(18)
Figure 2. Linear dependence of surface tension for three sections $x_{Sn}$:$x_{Ag}$:$x_{Cu}$ = 1:1:1, 1:1:2 and 1:2:1 using Kohler's model from 923 K to 1423 K.

**Kaptay equation.** The Kaptay equation\(^\text{22}\) is a modification of the Seetharaman-Du equation Sichen\(^\text{21}\), takes into account the theoretical relationship between the energy of cohesion alloys and the Gibbs activation energy of the viscous flow\(^\text{32}\). It has for expression:

\[
\eta = \frac{hNv}{\sum x_i V_i + \Delta V \exp \left[ \sum_i x_i \Delta G_i^c - \alpha \Delta H_{max} \right]} 
\]

(19)
where $\Delta V^E$ is the molar volume of excess for liquid quaternary alloys (m$^3$/mol) and $\Delta H_{\text{mix}}$ represent the integral enthalpy of the mixture, $\alpha$ is a semi-empirical parameter of the model. It is worth $(0.155 \pm 0.015)$ and can be neglected when experimental data are not available$^{32}$.

Most thermodynamic data of ternary and multicomponent systems will come from a theoretical calculation rather than direct experiences because of their difficulties especially for metallurgical systems. The geometric model has been applied to estimate the integral enthalpy of mixing. Chou$^{33}$ has presented a general geometric model for calculating the thermodynamic properties of ternary and multi-component systems from binary data$^{32}$.

Figure 3. Linear dependence of surface tension for three sections $x_{Sn}$-$x_{Ag}$-$x_{Cu}$ = 1:1:1, 1:1:2 and 1:2:1 using Toop's model from 923 K to 1423 K.
Figure 4. Comparison of experimental surface tensions (Moser et al.\textsuperscript{11} and Gancarz et al.\textsuperscript{14}) of the Sn-Ag-Cu-Bi quaternary system with the calculated ones (this work).

Table 5. Calculation square deviation values S between theoretical and experimental\textsuperscript{11,14} surface tension (N/m).
Results and Discussion

Surface tension in the liquid Sn-Ag-Cu-Bi quaternary alloys. The phase equilibria in the Sn-Ag-Bi-Cu quaternary system have been studied theoretically using thermodynamic calculations for three sections \(x_{\text{Sn}}:x_{\text{Ag}}:x_{\text{Cu}} = 1:1:1, 1:1:2\) and \(1:2:1\). The Gibbs energy values and the interaction parameters of all the phases of this system have been taken from NIST solder database\(^\text{34}\). The calculations were performed using Open Calphad software\(^\text{35}\).

As shown in Fig. 1, the results show that above 923 K, all the quaternary alloys of the three studied sections are in the liquid phase.

Figure 5. Linear dependences of Molar volume for three sections \(x_{\text{Sn}}:x_{\text{Ag}}:x_{\text{Cu}} = 1:1:1, 1:1:2\) and \(1:2:1\) using Kohler’s model in temperature range 923 K–1423 K.
One of the objectives of this article is to show that the geometric models and the Guggenheim equation work well for poly-constituent systems, especially for the quaternaries. Our calculations were done along three ternary sections Sn:Ag:Cu = 1:1:1, 1:1:2 and 1:2:1. In addition, (Sn-Ag-Cu)\texttext{eut} + Bi have been done using different predicting methods such as Kohler 15, Muggianu 16, Toop 17 and Hillert 18 models and Guggenheim equation 19 in the temperature range from 923 K to 1423 K.

The linear equations describing the temperature dependence of the surface tension for Sn-Ag-Cu-Bi quaternary alloys are illustrated in Figs 2 and 3 showing the results obtained according to Kohler and Toop models along three cross sections $x_{Sn}:x_{Ag}:x_{Cu} = 1:1:1, 1:1:2$ and $1:2:1$ over a wide range of temperatures, between 923 and 1423 K. For most of compositions of bismuth, the surface tension decreases with the increase of temperature, whereas...
Figure 7. Comparison of experimental density of the Sn-Ag-Cu-Bi quaternary alloys with those calculated values at different temperatures.

Table 6. Calculation square deviation values \( S \) between theoretical and experimental \(^{11,14} \) density (g/cm\(^3\)).
Bismuth addition in amount 0.1–0.2 mole an opposite tendency is observed $\sigma (T) > 0$, especially for section $x_{Sn}:x_{Ag}:x_{Cu} = 1:1:2$. The same results were obtained with Muggianu and Hillert models.

The surface tension of Sn-Ag-Cu-Bi quaternary alloys decreases as a function of Bismuth in the composition range $0.1 \leq x_{Bi} \leq 0.7$. While with a Bi addition in the range of 80 to 90 atomic percent an opposite trend has been observed. It should be noted that a similar behavior has been previously reported by Kucharski and Fima for the binary Ag-Bi. The surface tension decreases with the increase of Bi in the binary Ag-Bi. The pure surface tension Bi lower than that of the pure Sn means that increasing the content of Bi in the Sn-Bi welds decreases their surface tension. This effect can be explained by the enrichment of Bi in the superficial layer. Since bismuth has the

| Alloy (at.%) | $\eta$ = $\exp \left( \frac{E}{RT} \right)$ |
|-------------|----------------------------------|
| $x_{Sn}:x_{Ag}:x_{Cu}:x_{Bi}$ = 1:1:1 | |
| 0.3334 | 0.3333 | 0.3333 | 0.0000 | 0.5565 | 12437.74 |
| 0.3000 | 0.3000 | 0.3000 | 0.1000 | 0.4421 | 12595.71 |
| 0.2666 | 0.2667 | 0.2667 | 0.2000 | 0.3981 | 12845.13 |
| 0.2000 | 0.2000 | 0.2000 | 0.4000 | 0.3559 | 12745.36 |
| 0.1666 | 0.1667 | 0.1667 | 0.5000 | 0.3457 | 12770.30 |
| 0.1334 | 0.1333 | 0.1333 | 0.6000 | 0.3406 | 11830.82 |
| 0.1000 | 0.1000 | 0.1000 | 0.7000 | 0.3409 | 10949.53 |
| 0.0666 | 0.0667 | 0.0667 | 0.8000 | 0.3485 | 9777.260 |
| 0.0334 | 0.0333 | 0.0333 | 0.9000 | 0.3704 | 8275.750 |
| 0.0000 | 0.0000 | 0.0000 | 1.0000 | 0.4453 | 6450.001 |
| $x_{Sn}:x_{Ag}:x_{Cu}:x_{Bi}$ = 1:1:2 | |
| 0.5000 | 0.2500 | 0.2500 | 0.0000 | 0.4906 | 11539.83 |
| 0.4500 | 0.2250 | 0.2250 | 0.1000 | 0.4045 | 11581.40 |
| 0.4000 | 0.2000 | 0.2000 | 0.2000 | 0.3749 | 11647.91 |
| 0.3500 | 0.1750 | 0.1750 | 0.3000 | 0.3598 | 11631.28 |
| 0.3000 | 0.1500 | 0.1500 | 0.4000 | 0.3509 | 11481.63 |
| 0.2500 | 0.1250 | 0.1250 | 0.5000 | 0.3461 | 11165.70 |
| 0.2000 | 0.1000 | 0.1000 | 0.6000 | 0.3443 | 10650.23 |
| 0.1500 | 0.0750 | 0.0750 | 0.7000 | 0.3464 | 9926.916 |
| 0.1000 | 0.0500 | 0.0500 | 0.8000 | 0.3541 | 8987.113 |
| 0.0500 | 0.0250 | 0.0250 | 0.9000 | 0.3741 | 7835.113 |
| 0.0000 | 0.0000 | 0.0000 | 1.0000 | 0.4453 | 6450.001 |
| $x_{Sn}:x_{Ag}:x_{Cu}$ = 1:2:1 | |
| 0.2000 | 0.4000 | 0.4000 | 0.0000 | 0.6363 | 14083.91 |
| 0.1800 | 0.3600 | 0.3600 | 0.1000 | 0.4921 | 14167.05 |
| 0.1600 | 0.3200 | 0.3200 | 0.2000 | 0.4325 | 14258.51 |
| 0.1400 | 0.2800 | 0.2800 | 0.3000 | 0.3965 | 14250.19 |
| 0.1200 | 0.2400 | 0.2400 | 0.4000 | 0.3726 | 14067.28 |
| 0.1000 | 0.2000 | 0.2000 | 0.5000 | 0.3566 | 13626.64 |
| 0.0800 | 0.1600 | 0.1600 | 0.6000 | 0.3471 | 12903.32 |
| 0.0600 | 0.1200 | 0.1200 | 0.7000 | 0.3440 | 11839.13 |
| 0.0400 | 0.0800 | 0.0800 | 0.8000 | 0.3495 | 10425.75 |
| 0.0200 | 0.0400 | 0.0400 | 0.9000 | 0.3704 | 8538.246 |
| 0.0000 | 0.0000 | 0.0000 | 1.0000 | 0.4453 | 6450.001 |
| (Sn-Ag-Cu)+Bi | |
| 0.9678 | 0.0276 | 0.0046 | 0.0000 | 0.4151 | 7018.678 |
| 0.9237 | 0.0313 | 0.0048 | 0.0402 | 0.3894 | 7145.051 |
| 0.8971 | 0.0295 | 0.0053 | 0.0681 | 0.3863 | 7130.086 |
| 0.9613 | 0.0313 | 0.0074 | 0.0000 | 0.4118 | 7176.644 |
| 0.8808 | 0.0470 | 0.0086 | 0.0356 | 0.3753 | 8141.900 |
| 0.8951 | 0.0286 | 0.0101 | 0.0662 | 0.3848 | 7212.395 |
| 0.9425 | 0.0324 | 0.0075 | 0.0176 | 0.4244 | 7216.552 |
| 0.9330 | 0.0310 | 0.0005 | 0.0310 | 0.3921 | 7135.074 |

Table 7. Temperature dependence of the viscosity (mPa/s) of Sn-Ag-Cu-Bi quaternary alloys at various temperatures using Seetharaman-Sichen equation.
lowest surface tension of the four alloy metals ($\sigma_{\text{Bi}} < \sigma_{\text{Sn}} < \sigma_{\text{Ag}} < \sigma_{\text{Cu}}$), the system seems to reduce its energy by separating the component with the small surface tension at the surface. Indeed, the bismuth component plays an important role not only in reducing the melting temperature of the alloy but also in reducing the surface tension of the SnAgCuBi alloys. It is important to note that the same behavior was observed for the other models (Muggianu and Hillert) and the Guggenheim equation.

Our calculated surface tensions of five quaternary Sn-Ag-Cu-Bi alloys are illustrated in Fig. 4 together with the measured ones at 623 K–1123 K. It can be seen that a good agreement between the theoretical and measured values is obtained. In addition, for the comparison check, we calculated the mean square deviation corresponding to the experimental results for each traditional model and the Guggenheim equation.

| Alloy (at.%) | $\eta = \exp \left( \frac{A}{RT} \right)$ |
|-------------|-----------------------------|
| $x_{\text{Sn}} : x_{\text{Ag}} : x_{\text{Cu}} : x_{\text{Bi}} = 1:1:1$ |
| 0.3334 : 0.3333 : 0.3333 : 0.0000 | 0.6071 | 10849.77 |
| 0.3000 : 0.3000 : 0.3000 : 0.1000 | 0.4164 | 12720.42 |
| 0.2666 : 0.2667 : 0.2667 : 0.2000 | 0.3775 | 12911.64 |
| 0.2334 : 0.2333 : 0.2333 : 0.3000 | 0.3570 | 12911.64 |
| 0.2000 : 0.2000 : 0.2000 : 0.4000 | 0.3419 | 12803.56 |
| 0.1666 : 0.1667 : 0.1667 : 0.5000 | 0.3375 | 12379.54 |
| 0.1334 : 0.1333 : 0.1333 : 0.6000 | 0.3352 | 12379.54 |
| 0.1000 : 0.1000 : 0.1000 : 0.7000 | 0.3292 | 11323.66 |
| 0.0666 : 0.0667 : 0.0667 : 0.8000 | 0.3478 | 9594.35 |
| 0.0334 : 0.0333 : 0.0333 : 0.9000 | 0.3724 | 8059.59 |
| 0.0000 : 0.0000 : 0.0000 : 1.0000 | 0.4448 | 6449.17 |
| $x_{\text{Sn}} : x_{\text{Ag}} : x_{\text{Cu}} : x_{\text{Bi}} = 1:1:2$ |
| 0.5000 : 0.2500 : 0.2500 : 0.0000 | 0.4373 | 12180.01 |
| 0.4500 : 0.2250 : 0.2250 : 0.1000 | 0.3832 | 11664.54 |
| 0.4000 : 0.2000 : 0.2000 : 0.2000 | 0.3587 | 11697.79 |
| 0.3500 : 0.1750 : 0.1750 : 0.3000 | 0.3468 | 11622.97 |
| 0.3000 : 0.1500 : 0.1500 : 0.4000 | 0.3559 | 11082.56 |
| 0.2500 : 0.1250 : 0.1250 : 0.5000 | 0.3385 | 11074.24 |
| 0.2000 : 0.1000 : 0.1000 : 0.6000 | 0.3392 | 10525.52 |
| 0.1500 : 0.0750 : 0.0750 : 0.7000 | 0.3433 | 9768.95 |
| 0.1000 : 0.0500 : 0.0500 : 0.8000 | 0.3443 | 9012.37 |
| 0.0500 : 0.0250 : 0.0250 : 0.9000 | 0.3760 | 7613.12 |
| 0.0000 : 0.0000 : 0.0000 : 1.0000 | 0.4448 | 6449.17 |
| $x_{\text{Sn}} : x_{\text{Ag}} : x_{\text{Cu}} : x_{\text{Bi}} = 1:2:1$ |
| 0.2000 : 0.4000 : 0.4000 : 0.0000 | 0.5798 | 14624.32 |
| 0.1800 : 0.3600 : 0.3600 : 0.1000 | 0.4611 | 14449.73 |
| 0.1600 : 0.3200 : 0.3200 : 0.2000 | 0.4098 | 14449.73 |
| 0.1400 : 0.2800 : 0.2800 : 0.3000 | 0.3798 | 14386.59 |
| 0.1200 : 0.2400 : 0.2400 : 0.4000 | 0.3602 | 14117.17 |
| 0.1000 : 0.2000 : 0.2000 : 0.5000 | 0.3436 | 13701.47 |
| 0.0800 : 0.1600 : 0.1600 : 0.6000 | 0.3412 | 12828.50 |
| 0.0600 : 0.1200 : 0.1200 : 0.7000 | 0.3409 | 11722.74 |
| 0.0400 : 0.0800 : 0.0800 : 0.8000 | 0.3488 | 10259.47 |
| 0.0200 : 0.0400 : 0.0400 : 0.9000 | 0.3723 | 8422.08 |
| 0.0000 : 0.0000 : 0.0000 : 1.0000 | 0.4448 | 6449.17 |
| (Sn-Ag-Cu) + Bi |
| 0.9678 : 0.0276 : 0.0046 : 0.0000 | 0.4334 | 6523.16 |
| 0.9237 : 0.0313 : 0.0048 : 0.0402 | 0.4013 | 6607.13 |
| 0.8971 : 0.0295 : 0.0053 : 0.0681 | 0.3981 | 6590.57 |
| 0.9613 : 0.0313 : 0.0074 : 0.0000 | 0.4325 | 6622.93 |
| 0.8808 : 0.0720 : 0.0086 : 0.0386 | 0.3941 | 7383.66 |
| 0.8951 : 0.0286 : 0.0101 : 0.0662 | 0.3981 | 6627.09 |
| 0.9425 : 0.0324 : 0.0075 : 0.0176 | 0.4045 | 6555.89 |
| 0.9330 : 0.0310 : 0.0005 : 0.0310 | 0.4037 | 6600.48 |

Table 8. Temperature dependence of the viscosity (mPa/s) of Sn-Ag-Cu-Bi quaternary alloys at various temperatures using Kaptay equation.
where $\sigma_{th,i}$ and $\sigma_{exp,i}$ represent the surface tension of Sn-Ag-Cu-Bi alloys a permanent composition i for a theoretical models and an experimental values, respectively, while N is the total amount of investigate alloys. The calculations of square deviation are collected in Table 5.
Generally, the surface tensions calculated with Guggenheim equations are in good accord with those obtained experimentally. The calculated values from geometric models are slightly superior than the experimental ones. With the exception of certain temperatures, geometric models are in good accord with experimental data.

Molar volume in the liquid Sn-Ag-Cu-Bi quaternary alloys. The molar volume of Sn-Ag-Cu-Bi in the liquid phase over a wide temperature range (from 923 to 1423 K) was calculated using geometric models (Kohler, Muggianu, Toop and Hillert).

We give only the calculated results of the molar volume using the Kohler model (Fig. 5).
It can be noted in Fig. 5 that the molar volume of Sn-Ag-Cu-Bi augments linearly with the rise in temperature. Besides, the rise in the quantity of bismuth has an effect on the molar volume of Sn-Ag-Cu-Bi quaternary system. The similar behavior was observed for other models (Muggianu, Toop and Hillert).

Density in the liquid Sn-Ag-Cu-Bi quaternary alloys. The density of liquid Sn-Ag-Cu-Bi alloys as a function of temperature along the three sections $x_{\text{Sn}}:x_{\text{Ag}}:x_{\text{Cu}} = 1:1:1$, 1:1:2 and 1:2:1 was calculated from the molar volume. As an example, we present only the results of Kohler. The values are illustrated in the Fig. 6. The results obtained clearly show that the density of the quaternary Sn-Ag-Cu-Bi system decreases linearly with temperature $(\frac{\partial \rho}{\partial T} < 0)$ and increases with the concentration of Bismuth at a given temperature (Fig. 6). The increase in density with addition of Bi was observed. The same effect has been observed by other authors. This effect can be interpreted as bismuth having the most robust density as tin $(\rho_{\text{Sn}} < \rho_{\text{Bi}})$.

The calculated results are compared with those of Moser et al. and Gancarz et al. for (Sn 2.7 Ag 0.86 Cu 3.86 Bi, Sn 3.13 Ag 0.48 Cu 4.02 Bi, Sn 2.95 Ag 0.53 Cu 6.81 Bi and Sn 2.68 Ag 1.01 Cu 6.62 Bi) and (Sn 3.24 Ag 0.75 Cu 1.76 Bi) quaternary alloys, respectively (Fig. 7).

It can be noted simply from Fig. 7, our calculated density results in this study using the theoretical equation is in good accord with the experimental data. However, the geometric models are higher than experimental one. It may be concluded that the estimated density values for the quaternary Sn-Ag-Cu-Bi using theoretical equation are characteristics to ideal solution at different temperatures (623 K–1123 K).

Standard deviations were determined for all models and for theoretical equation as:

$$S = \frac{1}{N} \sqrt{\sum_{i=1}^{N} (\rho_{\text{th},i} - \rho_{\text{exp},i})^2}$$

where $\rho_{\text{th},i}$ and $\rho_{\text{exp},i}$ represent the density of Sn-Ag-Cu-Bi alloys a permanent composition $i$ for a theoretical models and an experimental values, respectively, while $N$ is the totality amount of investigate alloys. The calculations of square deviation are collected Table 6.

It can be seen from $S$ that the calculated values of the density using the (Toop and Hillert) models give results close to experimental values in particular for temperature range at 823–1123 K. While for temperature range 623 K–1123 K, the results calculated using the theoretical equation give the values closest to the experiment data.

Viscosity in the liquid Sn-Ag-Cu-Bi quaternary alloys. Based on Seetharaman-Sichen statistic and Kaptay equations for Sn-Ag-Cu-Bi alloys, viscosities were calculated. The theoretical results for the viscosity of Sn-Ag-Cu-Bi alloys obtained using Seetharaman-Sichen and Kaptay equations are presented in Tables 7 and 8, respectively as an Arrhenius equation at various temperatures and given away in Figs 8 and 9.

As seen from Fig. 8, the viscosity of these alloys decreases curvilinearly with increasing temperature and bismuth. This decrease of viscosity by adding bismuth can be explained by its low viscosity in comparison of the other metals $(\eta_{\text{Bi}} < \eta_{\text{Sn}} < \eta_{\text{Ag}} < \eta_{\text{Cu}})$.

The results show a similar behavior of the viscosity in function of the temperature than those obtained using Seetharaman-Sichen equation. The viscosity decreases curvilinear with increasing temperature, and decreases with function of temperature and Bi content for all sections (Fig. 9). The predicted results are compared to each other and to the experimental ones (Fig. 10).

As seen in Fig. 10, the viscosity values obtained by Seetharamn sichen and Kaptay equations are slightly lower than those measured by Gancarz et al. for Sn 3.24 Ag 0.75 Cu 1.76 Bi alloys.
Conclusions
In this work the some thermo-physical properties (Surface tension, molar volume, density and viscosity) of the quaternary system Sn-Ag-Cu-Bi have been predicted at different temperatures. Therefore, we reformulated models, which permit one to calculate the surface tension, molar volume and viscosity. This study is carried out using traditional geometric models and theoretical equation, such as Kohler, Muggianu, Toop and Hillert as symmetric and asymmetric models and Guggenheim, Seetharaman-sichen and Kaptay equations. Some important results of our predictions reveal the following conclusions:

- For all compositions of Bismuth (except for the composition range with Bismuth molar content lower than $x_{Bi} = 0.2$) in the quaternary system Sn-Ag-Cu-Bi, the surface tension decreases with increasing temperature. Indeed, the surface tension diminishes with addition of Bismuth concentration.
- Addition of Bismuth to ternary Sn-Ag-Cu increases the molar volume and density but diminishes the viscosity.
- We can conclude that among all the traditional predictive models and the theoretical equation, Guggenheim (for surface tension) and the theoretical equation (for viscosity) give the best agreement with the experimental one.
- The viscosity results of the present work obtained by Seetharaman sichen and Kaptay equations are slightly lower than those measured by Ganczarz et al.¹⁴.

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**Author Contributions**

Rachida M’CHAAR conceived of the presented idea and developed the theory and performed the computations. Professor Abdelaziz SABBAR verified the analytical methods. Professor Mouloud EL MOUDANE encouraged Rachida M’CHAAR to investigate Temperature dependences of surface tension, density and viscosity study of Sn–Ag–Cu with Bi additions using theoretical models and supervised the findings of this work. All authors discussed the results and contributed to the final manuscript. Rachida M’CHAAR developed the theoretical formalism, performed the analytic calculations and performed the numerical simulations. Both Abdelaziz SABBAR and Mouloud EL MOUDANE authors contributed to the final version of the manuscript. Abdelaziz Sabbar contributed to the design and implementation of the research, to the analysis of the results and to the writing of the manuscript.

**Additional Information**

**Competing Interests:** The authors declare no competing interests.

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