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Thermophysical Properties of Ag and Ag–Cu Liquid Alloys at 1098 K to 1573 K

Przemysław Fima · Natalia Sobczak

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Abstract The surface tension and density of liquid Ag and Ag–Cu alloys were measured with the sessile drop method. The sessile drop tests were carried out at temperatures from 1098 K to 1573 K, on cooling (temperature decreasing stepwise) under a protective atmosphere of high purity Ar (6N). The density of liquid Ag and Ag–Cu alloys decreases linearly with increasing temperature, and an increase in concentration of copper results in a lower density. The surface tension dependence on temperature can be described by linear equations, and the surface tension increases with increasing Cu content. The results of the measurements show good agreement with existing literature data and with thermodynamic calculations made using the Butler equation.

Keywords Ag–Cu alloys · Density · Sessile drop · Surface tension · Thermodynamic modeling

1 Introduction

Multicomponent alloys based on the Ag–Cu eutectic are widely utilized for joining ceramics, both oxides [1] and non-oxide ones [2], as well as metallic materials [3,4] using brazing techniques. Brazing processes can be numerically simulated to assess the applicability of the brazing alloy. These simulations require not only reliable values of thermophysical properties such as surface tension, density, and thermal expansion

P. Fima (✉) · N. Sobczak
Center for High Temperature Studies, Foundry Research Institute,
73 Zakopianska St., 30-418 Krakow, Poland
e-mail: pfima@iod.krakow.pl

P. Fima
Institute of Metallurgy and Materials Science, Polish Academy of Sciences,
25 Reymonta St., 30-059 Krakow, Poland

of liquid alloys, but also they should take into consideration the effects of different high-temperature phenomena accompanying brazing. For example, high brazing temperatures with Ag–Cu-based alloys (the melting temperature of the Ag–Cu eutectic is 1052 K) coupled with differences in coefficients of thermal expansion of liquid brazing alloys and ceramic-brazed parts cause different shrinkages and thus significant thermal stresses responsible for cracking of brazed joints. Moreover, the surface tension is a property of an alloy which is crucial in describing its wetting behavior on the surfaces of brazed parts.

In the past, the thermophysical properties of binary Ag–Cu alloys were investigated by a few research groups using different experimental methods and under varying conditions. A literature survey shows there is good agreement between density data of different authors [5–8], but there is scatter in the surface tension data [6,8–12]. A complex for investigations of high-temperature capillarity phenomena, developed in the Foundry Research Institute [13], has been recently used for accurate surface tension measurements of Sn [14] in the range of 523 K to 1023 K and AlTi-based alloys [15] at ~2000 K.

The aim of this study is to re-examine the surface tension, density, and thermal shrinkage of liquid Ag and Ag–Cu alloys at 1098 K to 1573 K with use of the above complex and to compare the results obtained with existing data as well as with thermodynamic calculations performed using the Butler equation.

2 Experimental

The surface tension and density of liquid Ag and three Ag–Cu alloys containing (0.3, 0.4, and 0.5) mole fraction of Cu was measured with the sessile drop method (SD) using the experimental complex for investigation of high-temperature capillarity phenomena. The complex, described in detail in [13], consists of a set of chambers allowing one to carry out the tests under a protective atmosphere of high-purity Ar (6N). High-purity Ag and Cu (5N) were used in this study. The samples were prepared by melting both metals, in proportions giving the desired compositions, in graphite crucibles under an Ar (6N) protective atmosphere. Directly before every test, each sample was cut into a cylinder of approximately 5 mm × 5 mm, ultrasonically cleaned in acetone, dried in air, and transferred into the test chamber. The mass of each sample was measured with an uncertainty of 0.0001 g before and after each test, and no mass change was observed. Well-polished, high-purity, and porosity-free graphite substrates were used as support in the sessile drop tests.

The sessile drop experiments were carried out under cooling in the temperature range of 450 K to 500 K above the liquids. The test started from heating to the maximum temperature, and after stabilization, the sample was kept at this temperature for 10 min. During that time, an image of the droplet was taken every 30 s, resulting in 20 images per the specific temperature. When the measurement was completed, the temperature was reduced to the next temperature, and the process was repeated on cooling until the sample reached the minimum measurement temperature. The magnification factor of the image in this study was found to be 19.5, and no image distortion was observed. For density determinations, digital pictures were processed by an image analysis software, and the obtained coordinates of points on the drop's surface were used to calculate the density [8]. For surface tension measurements, the drop images were processed using automatic computer calculation software ASTRA [16,17], and the density determined in the same experiment was used as an input parameter. The experimental uncertainty does not exceed 1 % for the density and 2.5 % for the surface tension.

3 Results and Discussion

3.1 Density

Figure 1 shows the results for the density of pure silver obtained in this study compared with selected literature data that are summarized together with corresponding conditions in Table 1. The results of density measurements presented in Fig. 2 were analyzed with the least squares method and the regressed linear equations are collected in Table 2 together with estimated errors and the calculated density at 1373 K (ρ_{1373}).

The analysis of the literature data shows that four main methods were applied for measurements of the density of liquid Ag, i.e., methods based on the Archimedes principle (A), the maximum bubble pressure method (MBP), the SD, and recently the electromagnetic levitation (EML) method. According to Table 1, the reported density of Ag at the melting point (ρ_L) varies from $9.15\,\mathrm{g \cdot cm^{-3}}$ [7] to $9.36\,\mathrm{g \cdot cm^{-3}}$ [23], whereas the thermal coefficient of the density (ρ_T) varies from $-0.00065\,\mathrm{g{\cdot}cm^{-3}{\cdot}K^{-1}}$ [5] to $-0.001175\,\mathrm{g \cdot cm^{-3} \cdot K^{-1}}$. Except for the slightly lower data of Brillo et al. [7] at the melting point, the data of different authors show very good agreement with each other, as the average value of ρ_L is $9.303\,\mathrm{g \cdot cm^{-3}}$, and the average ρ_T is $-0.000931\,\mathrm{g \cdot cm^{-3} \cdot K^{-1}}$.

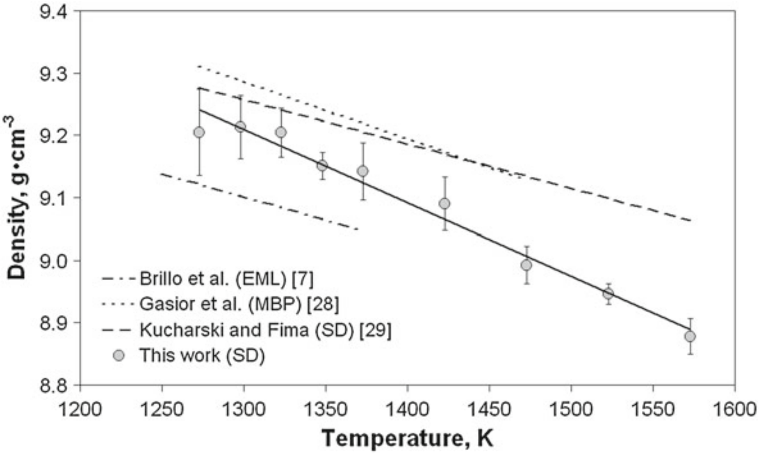

Fig. 1 Density of pure liquid Ag versus temperature, compared with literature data obtained in the past 10 years with three different methods: MBP [28], SD [29], and EML [7]

Table 1 Literature data for the density of pure liquid Ag together with the data of this study

ρ_L ($g \cdot cm^{-3}$)	ρ_T ($g \cdot cm^{-3} \cdot K^{-1}$)	Method	Atmosphere	Temperature (K)	Year	Reference
9.237	−0.00065	A	–	1273–1473	1929	[5]
9.28	−0.0009	A	–	1234–1573	1951	[18]
9.302	−0.000959	A	N_2	1234–1573	1953	[19]
9.348	−0.0011	MBP	H_2	1323–1423	1960	[20]
9.346	−0.0009067	A	–	1234–2450	1962	[21]
9.337	−0.00105	MBP	Ar	1234–1673	1964	[22]
9.36	−0.00108	MBP	Ar	1273–1473	1969	[23]
9.301	−0.00105	SD	Ar	1253–1381	1971	[24]
9.32	−0.00097	A	N_2 + 10% H_2	1234–1773	1972	[25]
9.321	−0.0009787	A	–	1234–1400	1975	[26]
9.31	−0.00078	SD	Ar, H_2	1234–1873	1989	[27]
9.346	−0.000911	MBP	Ar + 10% H_2	1273–1473	2003	[28]
9.304	−0.00071	SD	Ar	1273–1523	2005	[29]
9.15	−0.00074	EML	He + 8% H_2	1250–1380	2006	[7]
9.29	−0.001175	SD	Ar	1273–1573	2010	This study

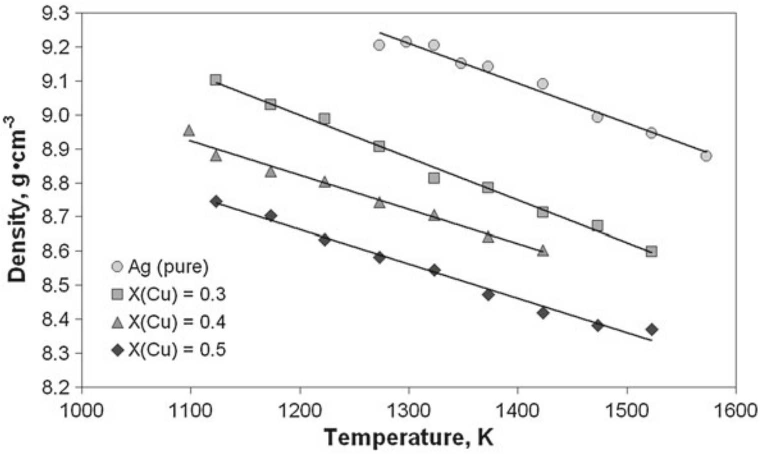

Fig. 2 Density data of liquid Ag–Cu alloys versus temperature

Table 2 Parameters of $(A - BT)$ of the temperature dependence of the density of liquid Ag–Cu alloys and extrapolated density values at 1373 K

X (Cu)	A ($g \cdot cm^{-3}$)	B ($10^{-4}\ g \cdot cm^{-3} \cdot K^{-1}$)	ρ_{1373} ($g \cdot cm^{-3}$)
0	10.738 ± 0.100	11.75 ± 0.71	9.12
0.3	10.499 ± 0.053	12.50 ± 0.40	8.78
0.4	10.032 ± 0.069	10.08 ± 0.55	8.65
0.5	9.867 ± 0.059	10.04 ± 0.45	8.49

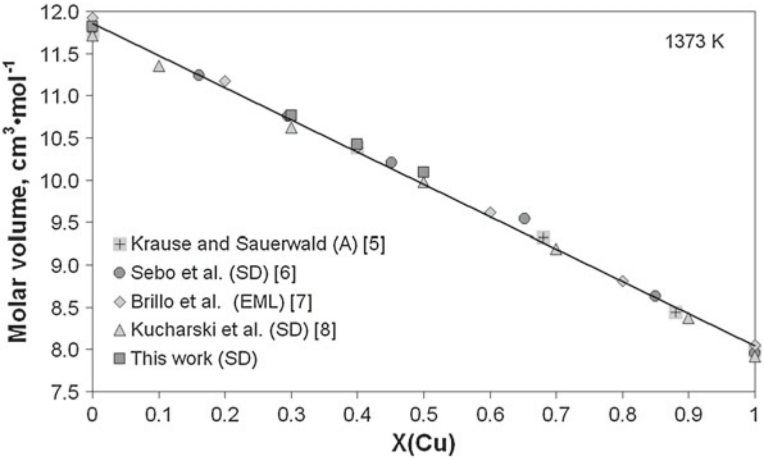

Fig. 3 Molar volume of liquid Ag–Cu alloys at 1373 K as a function of copper concentration in comparison to the data from [5–8]. *Line* presents linear regression of the data in the figure

Figure 1 shows the results of this study compared with the density data obtained with three different methods, published in the past 10 years [7,28,29]. Despite the differences in the thermal coefficient of density, our results are between the data of other authors. Also, the estimated errors of the parameters describing the density dependence on temperature are very similar.

From Fig. 2 it is evident that the increasing concentration of copper in the alloy results in a lower density. The thermal coefficients of density are similar for all of the investigated samples. The density of liquid Ag–Cu alloys was measured with three different methods: based on the Archimedes principle [5], the SD [6,8], and recently EML [7].

Based on the density data, the molar volume of Ag–Cu alloys was calculated with the use of the following equation, where $M_i, M_j, x_i, x_j, \rho_{i-j}, V_{i-j}$ are the atomic masses of the components, mole fractions of the components, density, and molar volume of the alloy, respectively.

$$V_{i-j} = \left(x_i M_i + x_j M_j\right)/\rho_{i-j} \tag{1}$$

In Fig. 3, the molar volume of Ag–Cu calculated at 1373 K is shown together with the results of earlier studies [5,7,8] at the same temperature and the data of Sebo et al. [6] obtained at 1381 K. It is evident that the present results are in good agreement with the data of other authors. According to Fig. 3, the molar volume of Ag–Cu alloys changes nearly linearly with composition, and hence it can be assumed to be close to the molar volume of the ideal solution.

3.2 Surface Tension

The surface tension for pure silver obtained in this study is presented in Fig. 4, together with some recent data of other authors. The surface tension of pure liquid silver was

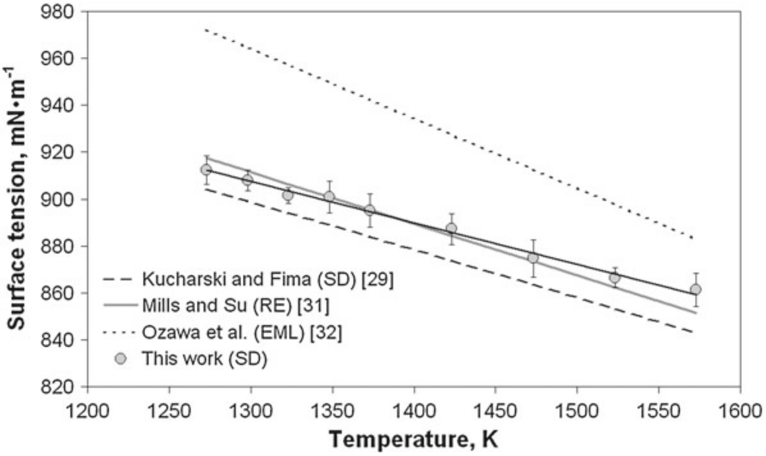

Fig. 4 Surface tension of pure liquid Ag versus temperature

measured by numerous authors. Some of those data, published before 1993, were collected by Keene [30], who, based on them, developed a linear equation describing the temperature dependence of the surface tension of liquid silver. Mills and Su [31] made an update to the data collected by Keene, and in the same way, calculated the averaged equation of the surface tension dependence on temperature taking into account the equation recommended by Keene. They found that newer data are within a 2 % limit of the equation recommended by Keene. It is clear from this figure that, despite the difference in the temperature coefficient, the data obtained in this study are very close to the equation recommended (RE) by Mills and Su [31]. Recent data of Ozawa et al. [32], measured with EML, are much higher than most of the data available in the literature [30]. The authors attributed this to very clean conditions (very low level of oxygen) in their apparatus.

The obtained experimental data for Ag–Cu alloys are shown in Fig. 5, and the corresponding linear equations are presented in Table 3. For all compositions the surface tension decreases linearly with increasing temperature. The surface tension increases with increasing content of Cu; however, it is accompanied with a decrease in the surface tension temperature coefficient. In general, our data are in good agreement with the results of other authors [6,8–12]. Most of the literature data were obtained with the SD, and only the data of Krause et al. [9] were obtained with the MBP. For alloys of high Cu content, as well as pure Cu, the data of Krause et al. [9] show a positive temperature coefficient, which is in contradiction to the data of other authors. The reason for this might be the contamination of the sample with surface active elements, most likely oxygen coming from a low purity protective atmosphere.

Lee et al. [11] examined the effect of oxygen on the surface tension of Ag–Cu alloys. They carried out experiments at 1373 K in the range of oxygen partial pressures from $p_{O_2} = 10^{-11}$ Pa to 10^{-3} Pa for three copper-rich alloys containing (0.8, 0.9, and 0.95) mole fraction of Cu, and for pure Ag and Cu. They found, in the range of oxygen partial pressures given above, the effect of oxygen on the surface tension is much stronger in the case of Cu, as the surface tension decreases steeply with increasing p_{O_2},

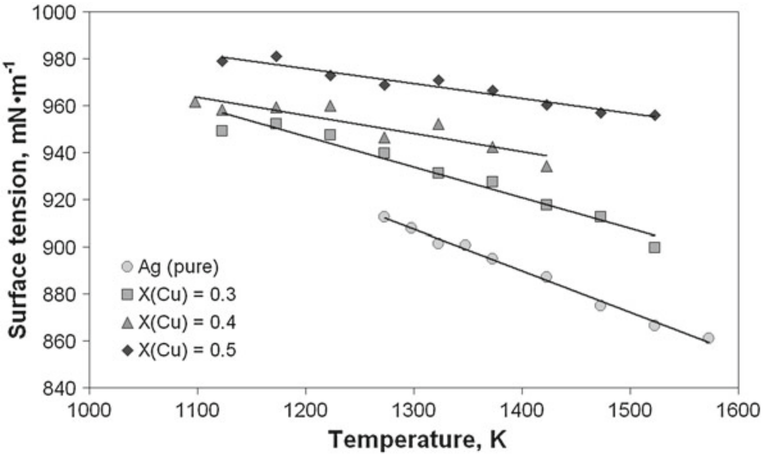

Fig. 5 Surface tension of Ag–Cu alloys versus temperature

Table 3 Parameters of $(A - BT)$ of the temperature dependence of the surface tension of liquid Ag–Cu alloys and extrapolated surface tension values at 1373 K

X (Cu)	A $(\mathrm{mN \cdot m^{-1}})$	B $(\mathrm{mN \cdot m^{-1} \cdot K^{-1}})$	σ_{1373} $(\mathrm{mN \cdot m^{-1}})$
0	1137 ± 8	0.176 ± 0.006	895
0.3	1103 ± 14	0.130 ± 0.011	924
0.4	1048 ± 18	0.077 ± 0.014	942
0.5	1052 ± 8	0.063 ± 0.006	965

compared to the slightly decreasing surface tension of Ag. This observation agrees very well with findings of other authors, for example, [33,34]. According to Lee et al. [11], the increasing concentration of Ag in Ag–Cu alloys changes its dependence on p_{O_2} by extending the range of relatively stable surface tension (decreasing slightly) to higher oxygen partial pressures. For example, they found that the alloy containing 0.8 mole fraction of Cu exhibits the same behavior in varying p_{O_2} as does pure Ag. Taking into account that the surface tension is, to a great extent, a property of the surface rather than the bulk, this finding was attributed to the enrichment of the surface of the alloy with Ag.

3.3 Thermodynamic Modeling

Assuming equilibrium between the bulk phase of a binary alloy and its surface layer which is treated as a separate "phase," the surface tension of the binary alloy can be described as

$$\sigma = \sigma_i + \frac{RT}{A_i} \ln \frac{x_i^{(s)}}{x_i} - \frac{1}{x_i} \left(G_i^{\mathrm{Ex}(s)} - G_i^{\mathrm{Ex}} \right) \tag{2}$$

where R, T, σ_i, A_i, $x_i^{(s)}$ are the universal gas constant, the absolute temperature, surface tension of component i, molar surface area of component i, and the mole fraction of component i in the surface layer, respectively. The surface area A_i is calculated from Avogadro's number N_0, the atomic mass, and density data, as follows

$$A_i = 1.091\ N_0\left(M_i/\rho_i\right)^{2/3} \tag{3}$$

This method of surface tension calculation was developed first by Butler [35] under the assumption that the difference in composition between the surface "phase" and the bulk phase is restricted to the first layer of molecules. The partial excess Gibbs energy of the component i in the bulk can be expressed in the form of Redlich–Kister polynomials [36]:

$$G_i^{\mathrm{Ex}} = \left(x_j\right)^2\left[L_{i-j}^{(0)} + L_{i-j}^{(1)}\left(x_j - 3x_i\right) + L_{i-j}^{(2)}\left(x_j - x_i\right)\left(x_j - 5x_i\right) + \cdots\right] \tag{4}$$

where L_{i-j}^{v} is the parameters that are dependent on temperature. There is an assumption that the absolute value of the partial excess Gibbs energy of a component in the surface layer ($G_i^{\mathrm{Ex}(s)}$) is smaller than that in the bulk phase (G_i^{Ex}) because atoms in the surface layer have lower coordination numbers than those in the bulk phase.

$$G_i^{\mathrm{Ex}(s)} = \beta G_i^{\mathrm{Ex}} \tag{5}$$

where β is an adjustable parameter. Some authors assume that the adjustable parameter is equal to the ratio of the coordination number of the surface atoms to the coordination number of the atoms in the bulk phase. Following Tanaka et al. [37], we take $\beta = 0.83$. The thermodynamic parameters L_{i-j}^{v} required for calculations were taken from the COST 531 thermodynamic database [38]. The surface tension and density for pure Cu were taken from refs. [31] and [8], respectively, while for Ag the data obtained in this study were used. The calculated surface tension of Ag–Cu alloys, at 1373 K, is compared to experimental data in Fig. 6. Figure 6 shows very good agreement between our results and the data of Novakovic et al. [12] as well as the results of our thermodynamic calculations.

Together with the surface tension, the composition of the surface layer of Ag–Cu alloys was calculated and it is presented in Fig. 7. As can be seen, the composition of the surface layer is significantly different from the composition of the bulk. The surface layer is enriched in silver as Ag is preferentially absorbed in the surface layer. For example, for a bulk composition of 0.2 mole fraction of Ag, the surface layer of the alloy contains 0.78 mole fraction of Ag. This agrees very well with 0.81 mole fraction of Ag calculated by Lee et al. [11].

4 Conclusion

The surface tension and density of liquid Ag and Ag–Cu alloys were measured by means of the SD under cooling from 1098 K to 1573 K. For all examined compositions, the density decreases linearly with temperature. A decrease in the density

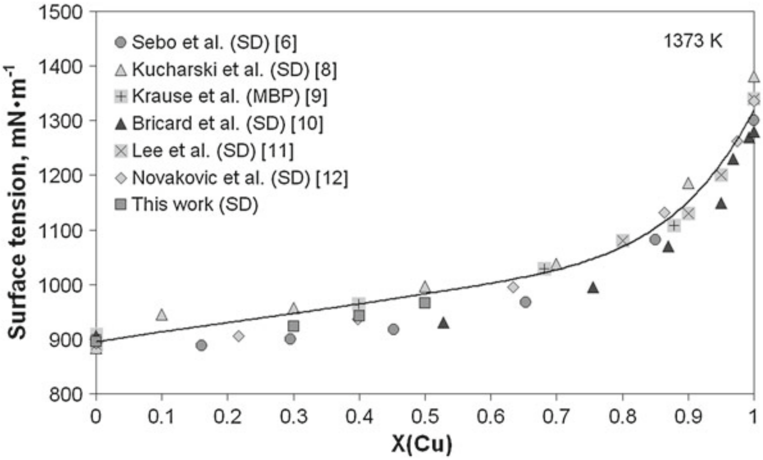

Fig. 6 Surface tension calculated from the Butler equation (*line*) at 1373 K compared with experimental data: this study and [6,8–12] (*points*)

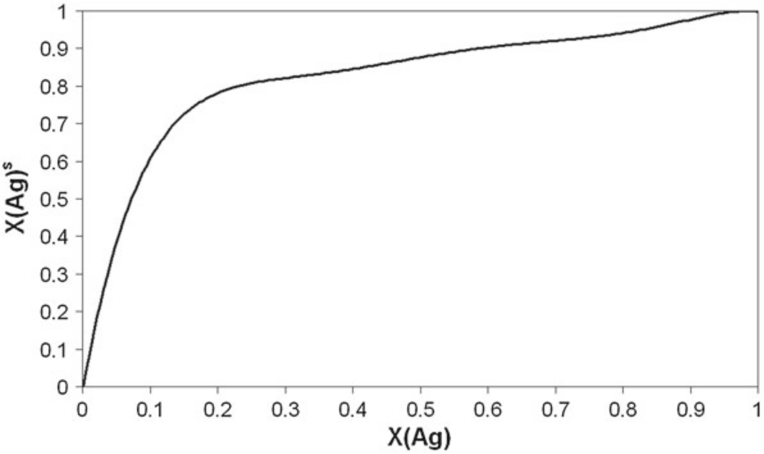

Fig. 7 Composition of the surface layer of liquid Ag–Cu alloys at 1373 K

was observed with increasing concentration of copper. The molar volume, calculated based on available literature data, was found to change nearly linearly with composition. The surface tension for pure silver and Ag–Cu alloys is a linear function of temperature, and it increases with increasing concentration of Cu. Our data agree very well with the data of other authors, and good agreement was found between our experimental data and thermodynamic calculations performed using the Butler equation.

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