# Analysis of literature models on viscosity of binary liquid metallic alloys on the example of the Cu-Ag system

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**Abstract**
The aim of this paper is to review all the existing literature models on the concentration dependence of the viscosity of binary liquid alloys and to check them against the measured viscosity values in the binary liquid Cu-Ag system at 1373K.

**Introduction**

Viscosity of binary and multi-component liquid alloys is one of the important parameters of materials processing. Unfortunately there are relatively few measured data on concentration dependence of liquid alloys, and the majority of them are obtained for low-melting point alloys, with some exceptions for liquid steel. That is why modeling the concentration and temperature dependence of liquid alloys viscosity is an important task. Modeling of viscosity of liquid alloys is usually done through thermodynamic properties of the alloys [1-8], although some papers are based also on different mixing rules [9-11]. Despite the fact that the history of modeling the viscosity of liquid alloys is more than 40 years old now [1], there is still no consensus in the research community, which equation of the published seven equations [1-8] is best to reproduce the experimental values. This situation can also be tracked from the fact that in the application papers, published recently, different models are applied by different research groups [12-16]. Our paper is written to discuss all the existing in the literature equations, and to check them against the measured viscosity data in one of the simplest system: the liquid binary Cu-Ag system.

**Literature models**

*The Moelwyn-Hughes equation* [1] takes into account that the viscous flow becomes more difficult when the cohesion energy of the alloy is increased:

$$\eta = (x_1 \cdot \eta_1 + x_2 \cdot \eta_2) \cdot \left(1 - 2 \cdot x_1 \cdot x_2 \cdot \frac{\Omega}{R \cdot T}\right) \tag{1}$$

where $\eta$ and $\eta_i$ - dynamic viscosity of the alloy and of pure phase i (i = 1, 2), (Pas),
$x_i$ – mole fraction of component i,
R = 8.314 J/molK, the universal gas constant,
T – absolute temperature (K),
$\Omega$ - the parameter of the of mixing of the alloy ($\Delta H = x_1 x_2 \Omega$), (J/mol).

*The Iida-Ueda-Morita equation* [2,3] takes into account theoretically the influence of the differences in atomic mass and size, and also the cohesion energy change due to alloy formation, through a semi-empirical parameter 0.12:

$$\eta = (x_1 \cdot \eta_1 + x_2 \cdot \eta_2) \cdot \left\{ 2 \cdot \left[ 1 + \frac{x_1 \cdot x_2 \cdot (\sqrt{m_1} - \sqrt{m_2})^2}{(x_1 \cdot \sqrt{m_1} + x_2 \cdot \sqrt{m_2})^2} \right]^{1/2} - 1 - \frac{5 \cdot x_1 \cdot x_2 \cdot (d_1 - d_2)^2}{x_1 \cdot d_1^2 + x_2 \cdot d_2^2} - \Delta \right\} \quad (2)$$

where $m_i$ – is the mass of the atom of component i, (kg),

$d_i$ – the double of Pauling's ionic radius of component i, (m),

$\Delta$ - is the thermodynamic correction, defined in two different ways [2, 3]:

$$\Delta = 0.12 \cdot \frac{\Delta H}{R \cdot T} \quad (2.a)$$

$$\Delta = 0.12 \cdot \frac{\Delta G^E}{R \cdot T} \quad (2.b)$$

where $\Delta G^E = \Delta H - T \Delta S^E$, i.e. the integral excess Gibbs energy, expressed through the heat of mixing ($\Delta H$) and excess entropy of mixing ($\Delta S^E$).

*The Kozlov equation* [4] is derived in a theoretical way, and finds for the first time the correlation in semi-logarithmic coordinates (compare with Eq-s (6-7)):

$$\ln \eta = \sum_{i=1}^{n} x_i \cdot \ln \eta_i - \frac{\Delta H}{3 \cdot R \cdot T} \quad (3)$$

*The Kucharski equation* [5] unfortunately uses a semi-empirical, ill-defined parameter $\alpha$, which can be found only from at least one measured data point:

$$\eta = x_1 \cdot \eta_1 \cdot \gamma_1^{\alpha} \cdot \frac{V_1}{V} \cdot V_1^* + x_2 \cdot \eta_2 \cdot \gamma_2^{\alpha} \cdot \frac{V_2}{V} \cdot V_2^* \quad (4)$$

where $\gamma_i$ – the activity coefficient of component i,

$\alpha$ - a fitting parameter,

$V_1, V_2$ – the molar volume of pure liquid metals 1 and 2 (m³/mol),

$V$ – the molar volume of liquid alloy (m³/mol),

$V_1^*$ and $V_2^*$ are parameters, written as [5]:

$$V_1^* = \left( \frac{x_1 \cdot V_1^{1/3} + x_2 \cdot V_2^{1/3}}{x_1 \cdot V_2^{1/3} + x_2 \cdot V_2 \cdot V_1^{-2/3}} \right)^2 \quad (4.a)$$

$$V_2^* = \left( \frac{x_1 \cdot V_1^{1/3} + x_2 \cdot V_2^{1/3}}{x_2 \cdot V_2^{1/3} + x_1 \cdot V_2^{-1} \cdot V_1^{4/3}} \right)^2 \quad (4.b)$$

*The Hirai equation* [6] is a semi-empirical extrapolation of the Andrade's equation, suggested originally for pure liquid metals:

$$\eta = 1.7 \cdot 10^{-7} \cdot \frac{\rho^{2/3} \cdot T_m^{1/2}}{M^{1/6}} \cdot \exp\left[ \frac{2.65 \cdot T_m^{1.27}}{R} \cdot \left( \frac{1}{T} - \frac{1}{T_m} \right) \right] \quad (5)$$

where  $\rho$ - density of the alloy (kg/m$^3$),

M – average atomic weight of the alloy (kg/mol),

T$_m$ – melting point, i.e. liquids temperature of the alloy (K).

*The Seetharaman-Du Sichen equation* [7] is based on the Eyring equation, with describing the activation energy of the alloy by the semi-empirical Eq.(6.a), contradicting the majority of the previous models (see Eq-s (1, 2, 3)):

$$\eta = h \cdot N_{Av} \cdot \frac{\rho}{M} \cdot \exp\left(\frac{\Delta G^*}{R \cdot T}\right)$$ (6)

where  $\rho$ - density of the alloy (kg/m$^3$), calculated additively way from pure components,

h – is the Planck constant (6.626 10$^{-34}$ J s),

N$_{Av}$ – is the Avogadro number (6.022 10$^{23}$ 1/mol),

$\Delta G^*$ - the Gibbs energy of activation of the viscous flow (J/mol) defined as [7]:

$$\Delta G^* = \sum_{i=1}^{2} x_i \cdot \Delta G_i^* + R \cdot T \cdot \sum_{i=1}^{2} x_i \cdot \ln x_i + 3 \cdot R \cdot T \cdot x_1 \cdot x_2 + \Delta H - T \cdot \Delta S^E$$ (6.a)

$\Delta G_i^*$ – the Gibbs energy of activation of the viscous flow in pure component i:

$$\Delta G_i^* = R \cdot T \cdot \ln\left(\frac{\eta_i \cdot M_i}{h \cdot N_{Av} \cdot \rho_i}\right)$$ (6.b)

*The Kaptay equation* [8] is a modification of Eq.(6), taking into account the theoretical relationship between the cohesion energy of the alloy and the activation energy of viscous flow, and also being in a qualitative agreement with the majority of the previous thermodynamic models (see Eq-s (1, 2, 3)), stating that in alloys with stronger cohesion energy the viscosity will increase, and not decrease:

$$\eta = \frac{h \cdot N_{Av}}{\sum_i x_i \cdot V_i + \Delta V^E} \cdot \exp\left[\frac{\sum_i x_i \cdot \Delta G_i^* - (0.155 \pm 0.015) \cdot \Delta H}{R \cdot T}\right]$$ (7)

where  $\Delta V^E$ – the excess molar volume upon alloy formation (m$^3$/mol).

**Application of the models to the liquid Cu-Ag system at 1373 K**

The models were checked against the well accepted experimental data, measured by Gebhardt and Wörwag [17]. The model parameters for pure liquid metals are given in Table 1. The phase diagram and thermodynamic properties of the alloys were taken from [18]. As follows from thermodynamic properties, there is a weak positive deviation from the Raoult's rule in the system. The excess molar volume of the alloy was taken as zero, due to lack of experimental data. The models, given above are compared with the measured data in Fig-s 1-6. The Kucharski's model is not shown, due to the semi-empirical parameter $\alpha$..

Table 1. Parameters of the models at 1373 K

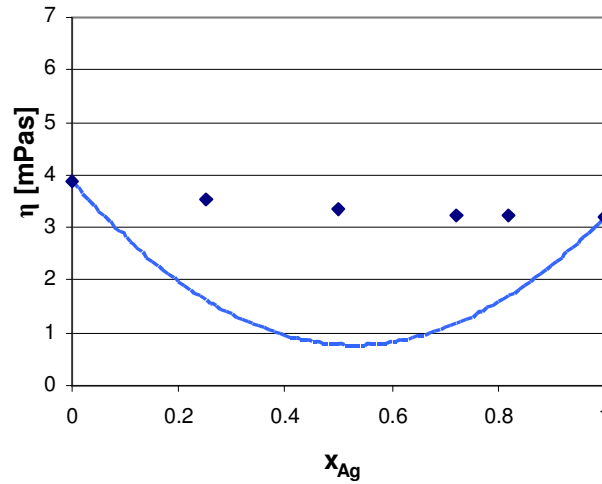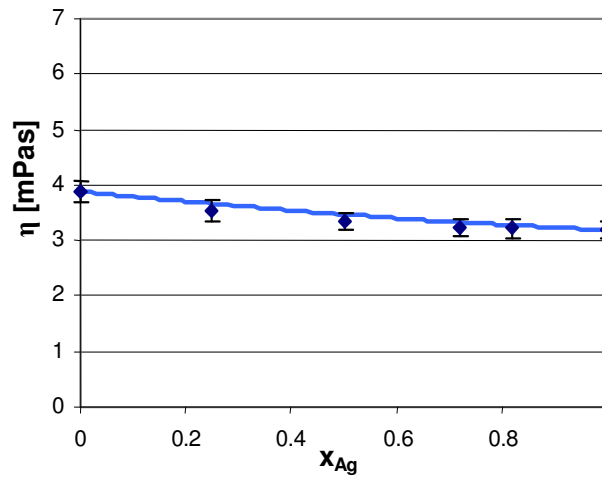| Components | $\eta_i$ [mPas] | $V_i$ [cm$^3$/mol] | $\rho_i$ [kg/m$^3$] | $d_i$ [m] |
|---|---|---|---|---|
| Cu | 3,9 | 8,09 | 7847 | $1,96*10^{-10}$ |
| Ag | 3,19 | 11,72 | 9185 | $2,52*10^{-10}$ |



Fig. 1. Viscosity of Cu-Ag alloys at 1373K, measured points [17], line calculated by Eq.(1)



Fig. 2. Viscosity of Cu-Ag alloys at 1373K, measured points [17], line calculated by Eq.(2)
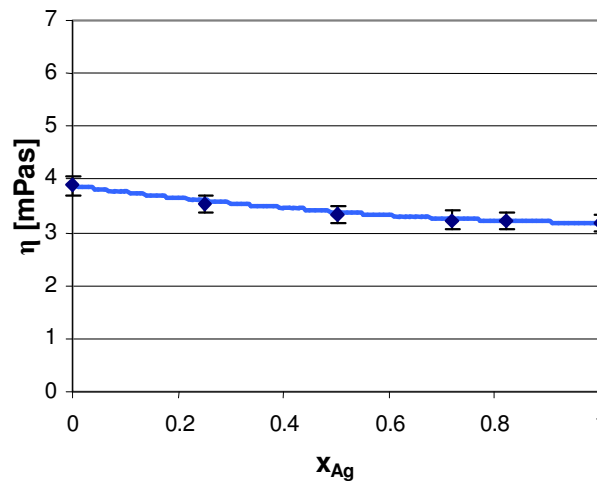


Fig. 3. Viscosity of Cu-Ag alloys at 1373K, measured points [17], line calculated by Eq.(3)
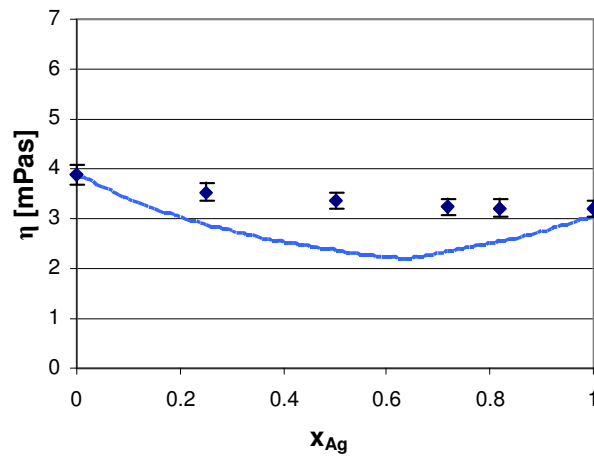
Fig. 4. Viscosity of Cu-Ag alloys at 1373K, measured points [17], line calculated by Eq.(5)
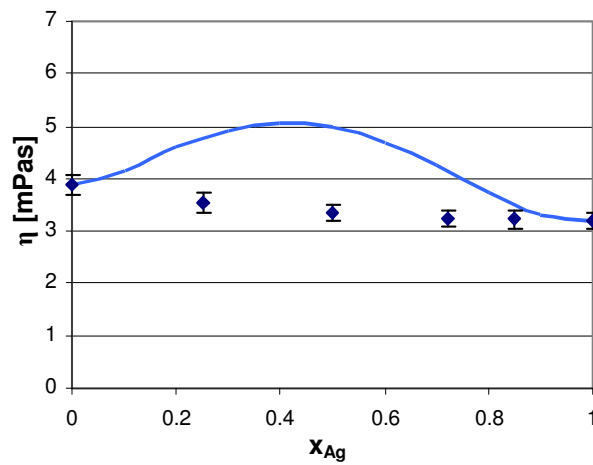


Fig. 5. Viscosity of Cu-Ag alloys at 1373K, measured points [17], line calculated by Eq.(6)
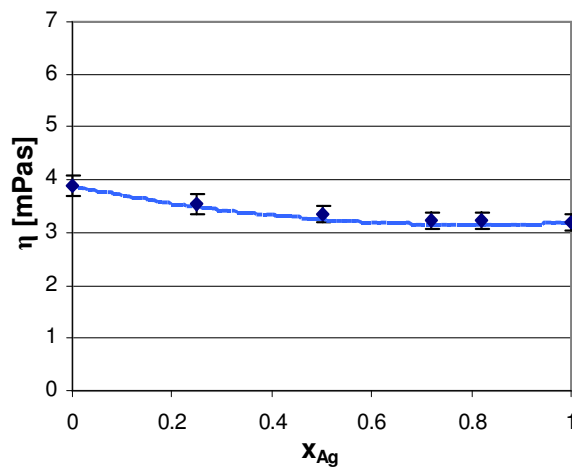


Fig. 6. Viscosity of Cu-Ag alloys at 1373K, measured points [17], line calculated by Eq.(7)

## Discussion of the results

From the concentration dependence of the measured viscosity data one can see that the excess viscosity shows a slight negative deviation from additivity, being in agreement with the slight positive values of the heat of mixing of the alloys (while the viscosity values of the pure components are very similar), according to Eq-s (1, 2, 3, 7), and being in contradiction with Eq.(6). Among Eq-s (1, 2, 3, 7) the coefficient, used in Eq.(1) is obviously too large, contradicting the experimental data. Data, calculated by Eq.(5) are also in a relatively good agreement with experimental points.

## Conclusions

In this paper seven equations, published in the literature have been shortly discussed and checked against the measured data for the Cu-Ag binary liquid alloys system at 1373K, measured in [17]. Based on this single system, one can conclude that the models due to Iida-Ueda-Morita [2, 3], to Kozlov [4], and to Kaptay [8] are able to reproduce measured data with a reasonable accuracy. The models due to Moelwyn-Huges [1], and to Hirai [6] describe the character of the experimental data correctly but their magnitude differs significantly. The Kucharski-model [5] cannot be applied without a system-dependent semi-empirical parameter, while the Seetharam-Du-Sichen model [7] predicts the excess viscosity of a wrong sign. The above equations should be checked against more systems to make the final conclusion on the ability of this or that model to reproduce the concentration dependence of the viscosity of multi-component alloys from their excess thermodynamic properties.

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