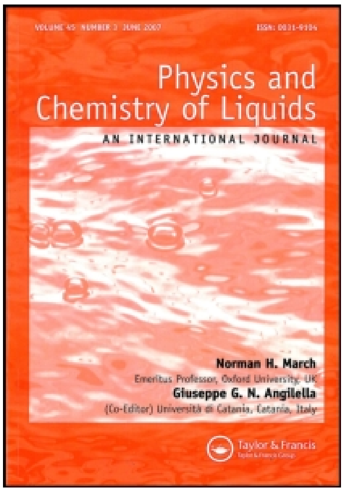

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Surface tension, viscosity and concentration fluctuations in liquid Ag-In-Sn

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Surface tension, viscosity and concentration fluctuations in liquid Ag–In–Sn

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The surface tension and the viscosity of the liquid system Ag–In–Sn are calculated by using the thermodynamic activities as input data. Both quantities exhibit highly non-linear variations with the concentration. The surface tension is discussed in terms of the deviations of the long-wavelength limit of the concentration–concentration fluctuations $S_{cc}(0)$ from ideality with special emphasis on the equiatomic section $c_{In}/c_{Sn} = 1$. The marked deviations found for $S_{cc}^{AgAg}(0)$ hint at the increased segregation of Ag-atoms from the surface into the bulk for $c_{Ag} < 0.5$ and the recovered tendency to stay on the surface at compositions $c_{Ag} > 0.5$. The results on $S_{cc}^{SnSn}(0)$ are $S_{cc}^{InIn}(0)$ also included in the discussion. The viscosity exhibits negative deviations from ideality following the very particular variation of the excess free energy of mixing with the composition which is also the characteristic feature of the binary Ag-based systems.

Keywords: Ternary alloy; Concentration fluctuations; Viscosity

1. Introduction

In view of serious environmental problems associated with the excessive use of conventional Pb-containing solders, in the recent past increased attention has been given to the development and the improvement of Pb-free solder materials. Since a good wetting behaviour is one of the most important physical requirements for practical use the surface tension of the liquid solder has become one of the key factors. The majority of the potential candidates are multicomponent systems based on Sn alloyed with In, Zn, Sb and smaller amounts of Cu, Ag or even Au [1].

In order to provide the thermodynamic database of these systems the thermodynamic properties of liquid Cu–Sn–In and Ag–Sn–In have been investigated [2–4]. This article concentrates on the surface tension and the viscosity of liquid Ag–In–Sn by combining the experimental free energy of mixing with Butler's model of surface tension [5] and the model of viscosity put forward by Seetharaman and Du Sichen [6].

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The binaries Ag–In, Ag–Sn and In–Sn are both experimentally and theoretically well characterized [7–12], but excepting the very specific surface tension measurements focused on near-eutectic AgInSn (Sn-3.8at%Ag with small additions of In [4]) the variation of the physical properties under consideration over the entire ternary phase filed is now known. In this article, special emphasis will be placed on the interplay between the surface tension and the long-wavelength limit of the Bhatia–Thornton structure factors $S_{cc}^{ij}(0)$ which give valuable information on the local structure and the concentration fluctuations occurring in the system [13].

Judged by the thermodynamic properties the binary systems involved in the investigation exhibit particular features [14]. In liquid Ag–In and Ag–Sn the heat of mixing and the excess entropy of mixing pass through pronounced minima located at higher concentrations of Ag followed by a more or less pronounced trend to positive values for high concentration of In or Sn. The resulting inflection point in the excess free energy of mixing is a typical feature of both systems. In In–Sn the heat of mixing is extremely small and the excess entropy changes sign from negative on the In-side to positive on the Sn-side. It was interesting to find out how this exceptional thermodynamic behaviours affect the physical properties of the system.

2. Method

All the evaluations performed in this article were based on the free energies of mixing G^{m} reported in the literature [4,14]. Due to the marked temperature dependence of the thermodynamic quantities of the binary systems – in particular those of Ag–Sn – it was difficult to find a common reference temperature where the three binaries are experimentally well established. From mass spectrometry studies Miki *et al.* [3] obtained results for both the binary systems and the ternary system in the temperature range from 1273–1573 K. However, this is too far above the experimental range of surface tension and viscosity measurements which are in general performed up to some hundred degrees above the liquidus. Therefore, the reference temperature was taken as 973 K which was considered to be an acceptable compromise between the reference temperatures selected by Hultgren *et al.* [14] for the binary systems (1100 K for Ag–In, 900 K for Ag–Sn and 700 K for In–Sn). The excess free energies of mixing G^{xs} of the binaries were transformed to 973 K by combining the heat of mixing H^{m} with the excess entropy term $T \cdot S^{xs}$ assuming that both H^{m} and S^{xs} are constant at least within around 100–200 K.

According to the phase relationships at 973 K [4] the boundary of the liquid phase lies around $c_{Ag} \approx 0.7$, therefore all values cited for compositions $c_{Ag} > 0.7$ have only hypothetical character. Throughout the article the compositions c_i are given as atomic fractions. For practical application the multi-parameter model of Lee *et al.* [15] was applied to represent the excess free energy of mixing

$$\frac{G^{xs}}{RT} = \sum_{i=1}^{3} \sum_{j>1}^{3} c_i c_j \left\{ a_1^{ij} c_i + a_2^{ij} c_j + c_i c_j (a_3^{ij} c_i + a_4^{ij} c_j) \right\} + c_1 c_2 c_3 \sum_{k=1}^{3} a_k^{123} c_k \qquad (1)$$

The binary parameters a_k^{ij} were obtained by fitting equation (1) to the thermodynamic data selected for the binary systems. For the ternary part the parameters a_k^{123} assessed by Liu *et al.* [4] were employed.

As regards the surface tension, Butler [5] assumed that the chemical potential of each species in the surface layer equals its chemical potential in the bulk plus the surface energy. The change in surface tension (from σ_i to σ) due to alloying is related to the compositions (c_i, c_i^{m}) and the thermodynamic activity coefficients (γ_i, γ_i^{m}) via

$$\sigma = \sigma_i + \frac{RT}{s_i}\ln\frac{c_i^{\mathrm{m}}}{c_i} + \frac{RT}{s_i}\ln\frac{\gamma_i^{\mathrm{m}}}{\gamma_i} \tag{2}$$

The subscript i refers to the i-th component of the alloy, c_i and γ_i denote the atomic fraction and the activity coefficient in the bulk, c_i^{m} and γ_i^{m} are those in the surface monolayer. The molar surface area s_i can be related to the molar volume V_i of the pure liquid [16]

$$s_i = b \cdot N_{\mathrm{A}}^{1/3} \cdot V_i^{2/3} \tag{3}$$

The geometric factor b was taken as 1.091 which is a value representative of close packed structures [17]. The molar volumes were those compiled by Crawley [18].

The activity coefficients are defined by the derivative of the free energy of mixing G^{m} with respect to the composition c_i according to

$$\ln\gamma_i = \frac{1}{RT}\cdot\left(\frac{\partial G^{\mathrm{m}}}{\partial c_i}\right)_{P,T,c} - \ln c_i \tag{4}$$

Values of $\ln\gamma_i$ can be obtained either by numerical differentiation of G^{m} or from the analytical expressions obtained by combining equation (4) with equation (1). The results are given elsewhere [15].

Assuming that the excess free energy is due to pair-wise interactions between the constituent atoms the activity coefficients γ_i and γ_i^{m} can be related to their respective coordination numbers z and z^{m}

$$\ln\gamma_i^{\mathrm{m}} / \ln\gamma_i = z^{\mathrm{m}}/z \tag{5}$$

For close packed solid structures the respective coordination numbers of $z = 12$ and $z^{\mathrm{m}} = 9$ give a ratio of $z^{\mathrm{m}}/z \approx 0.75$ which is suggested to be a good estimate for densely packed liquid structures [19].

Equation (2) holds for each particular constituent of the system, therefore the solution of the problem is to find the set of surface concentrations $(c_1^{\mathrm{m}}, c_2^{\mathrm{m}}, c_3^{\mathrm{m}})$ which together with the respective activity coefficients satisfies all three equations simultaneously. The surface tensions of the elements at the reference temperature were taken from the compilation of Iida and Guthrie [20].

The calculation of the viscosity η was based on the formula proposed by Seetharaman and Du Sichen [6]

$$\eta = \left(\frac{h\rho N_{\mathrm{A}}}{M}\right)\cdot\exp\left(\frac{G^{*}}{RT}\right) \tag{6}$$

where ρ is the density of the alloy, M the molar mass N_A, R and h have their usual meanings. The activation energy of the viscous flow G^* in a multicomponent system is assumed to be given by the activation energies of the pure constituents G_i^*, and the free energy of mixing G^m of the system according to

$$G^* = \sum_i c_i G_i^* + G^m + 3RT \cdot \sum_{i,j(i>j)} c_i c_j \tag{7}$$

At the given reference temperature of 973 K the input data used in this article were $G_{\mathrm{Ag}}^* = 42.24\,\mathrm{kJ\,mol^{-1}}$, $G_{\mathrm{In}}^* = 28.50\,\mathrm{kJ\,mol^{-1}}$ and $G_{\mathrm{Sn}}^* = 30.14\,\mathrm{kJ\,mol^{-1}}$ [6].

According to the expressions worked out by Bhatia and Ratti [21] for the case of multicomponent systems the long-wavelength limit of the concentration–concentration structure factors $S_{cc}^{ij}(0)$ in a ternary system are given as

$$S_{cc}^{ij}(0) = \frac{N_A k_B T G^{ij}}{G_{ii} \cdot G_{jj} - G_{ij} \cdot G_{ij}} \tag{8}$$

The quantities G_{ij} are related to the second derivatives of the free energy of mixing G^m with respect to the alloy compositions

$$G_{ij} = \left(\frac{\partial^2 G^m}{\partial c_i \partial c_j} \right)_{\mathrm{P,T,c'}} \tag{9}$$

The subscript c′ indicates that the compositions not involved in the differentiation are held constant. G^{ij} is the cofactor of the element G_{ij} in the matrix of the G_{kl}-elements. Physically, $S_{cc}^{ii}(0)$ is a measure of the mean square fluctuation in the concentration of the i-th species $\langle (\Delta c_i)^2 \rangle$ while $S_{cc}^{ij}(0)$ refers to the correlation $\langle \Delta c_i \Delta c_j \rangle$ between the fluctuations in c_i and c_j.

3. Results and discussion

The simultaneous solution of equation (2) ($i = 1, 2, 3$ for Ag, In, Sn) yields the surface tension of the alloy (figure 1) and the concentrations of the constituents in the surface layer ($c_{\mathrm{Ag}}^m, c_{\mathrm{In}}^m, c_{\mathrm{Sn}}^m$). Judged by the surface tension of the pure components a high surface concentration of Ag stands for a high surface energy ($\sigma_{\mathrm{Ag}} = 1.016\,\mathrm{mN\,m^{-1}}$) whereas a likewise low surface energy is to be expected for high surface concentrations of In ($\sigma_{\mathrm{In}} = 0.507\,\mathrm{mN\,m^{-1}}$) or Sn ($\sigma_{\mathrm{Sn}} = 0.518\,\mathrm{mN\,m^{-1}}$).

The most marked result of the calculations is the extremely low concentration of Ag-atoms in the surface layer (figure 2). Excepting the alloys with a very high content of Ag ($c_{\mathrm{Ag}} > 0.9$) the majority of Ag atoms is found to be segregated from the surface into the bulk. Even for contents as much as $c_{\mathrm{Ag}} < 0.5$ the concentration on the surface is found to be less than 2 at% ($c_{\mathrm{Ag}}^m < 0.02$). As a result, the surface tension is primarily determined by In and Sn and remains thus low over an extremely wide range of compositions (figure 1). The experimental point of $(0.506 \pm 0.008)\,\mathrm{mN\,m^{-1}}$ obtained near the Sn-3.8at%Ag eutectic ($c_{\mathrm{In}} = 0.1$) fits roughly into the picture, although the authors claimed some disagreement with the theory [4].

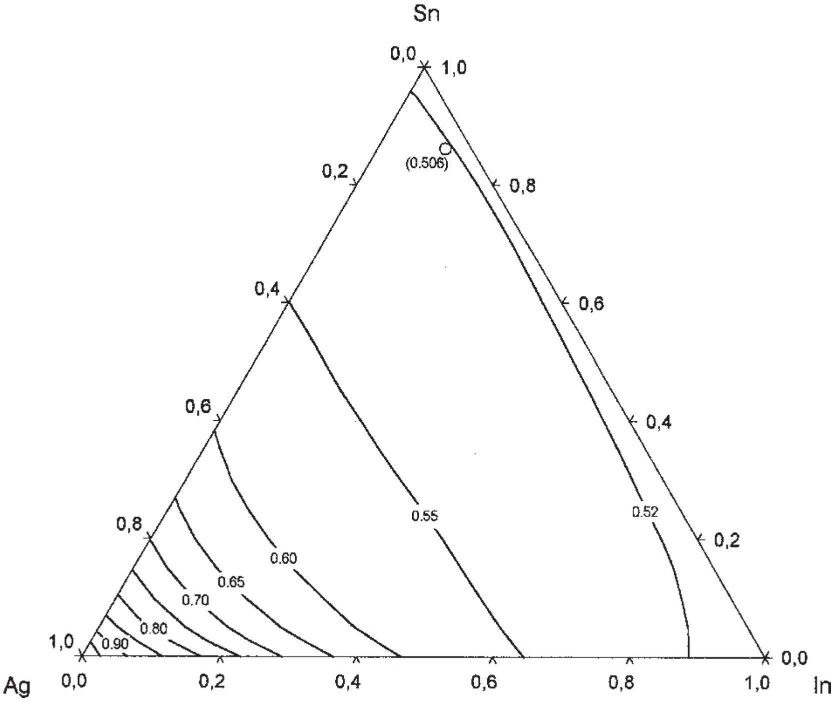

Figure 1. Surface tension of liquid Ag–In–Sn at 973 K.

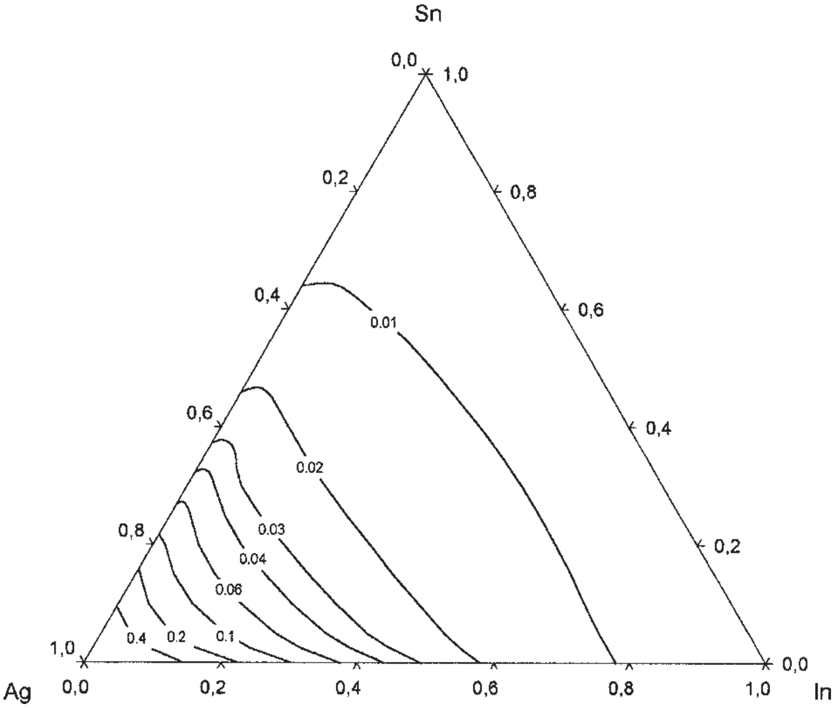

Figure 2. Surface concentration of Ag in liquid Ag–In–Sn at 973 K.

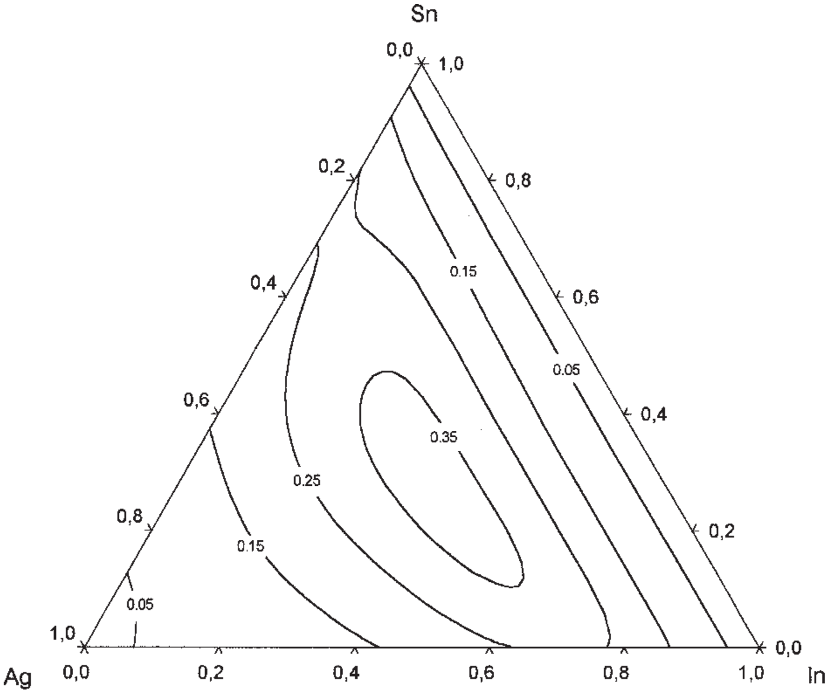

Figure 3. Concentration–concentration fluctuations $S_{\mathrm{cc}}^{\mathrm{AgAg}}(0)$ in liquid Ag–In–Sn at 973 K.

Bhatia and March [22] suggested a reciprocal relationship between the surface tension and the concentration–concentration fluctuations $S_{\mathrm{cc}}(0)$ in binary systems. For ternary systems the argumentation is more intricate, because there are more partial structure factors to be included in the discussion: $S_{\mathrm{cc}}^{\mathrm{AgAg}}(0)$, $S_{\mathrm{cc}}^{\mathrm{AgIn}}(0)$, $S_{\mathrm{cc}}^{\mathrm{AgSn}}(0)$, $S_{\mathrm{cc}}^{\mathrm{InIn}}(0)$, $S_{\mathrm{cc}}^{\mathrm{InSn}}(0)$ and $S_{\mathrm{cc}}^{\mathrm{SnSn}}(0)$. The variations of $S_{\mathrm{cc}}^{\mathrm{AgAg}}(0)$, $S_{\mathrm{cc}}^{\mathrm{InIn}}(0)$ and $S_{\mathrm{cc}}^{\mathrm{SnSn}}(0)$ over the ternary phase field are represented in figures 3–5. The maxima of the fluctuations are located in the central portion of the phase field ($c_{\mathrm{Ag}} \approx 0.35$, $c_{\mathrm{In}} \approx c_{\mathrm{Sn}}$) indicating that in this range of composition the surface energy can easily be minimized by the desorption of Ag-atoms from the surface into the bulk and conversely by the preferential migration of In- and Sn-atoms into the surface layer.

So far the interpretation is reasonable, however, it has to be stressed that even for an ideal mixture where

$$\begin{aligned} G^{\mathrm{xs}} &= 0 \\ G^{\mathrm{id}} &= -R \cdot \sum c_i \ln c_i \\ \gamma_i &= \gamma_i^{\mathrm{m}} = 1 \\ S_{\mathrm{cc}}^{ij,\mathrm{id}}(0) &= -c_i \cdot c_j \quad \text{for} \quad i \neq j \\ S_{\mathrm{cc}}^{ii,\mathrm{id}}(0) &= -c_i \cdot (1 - c_i) \end{aligned} \tag{10}$$

the surface layer would be depleted from Ag and enriched in In and Sn. This is simply the result of the balance between the requirement to minimize the surface energy and

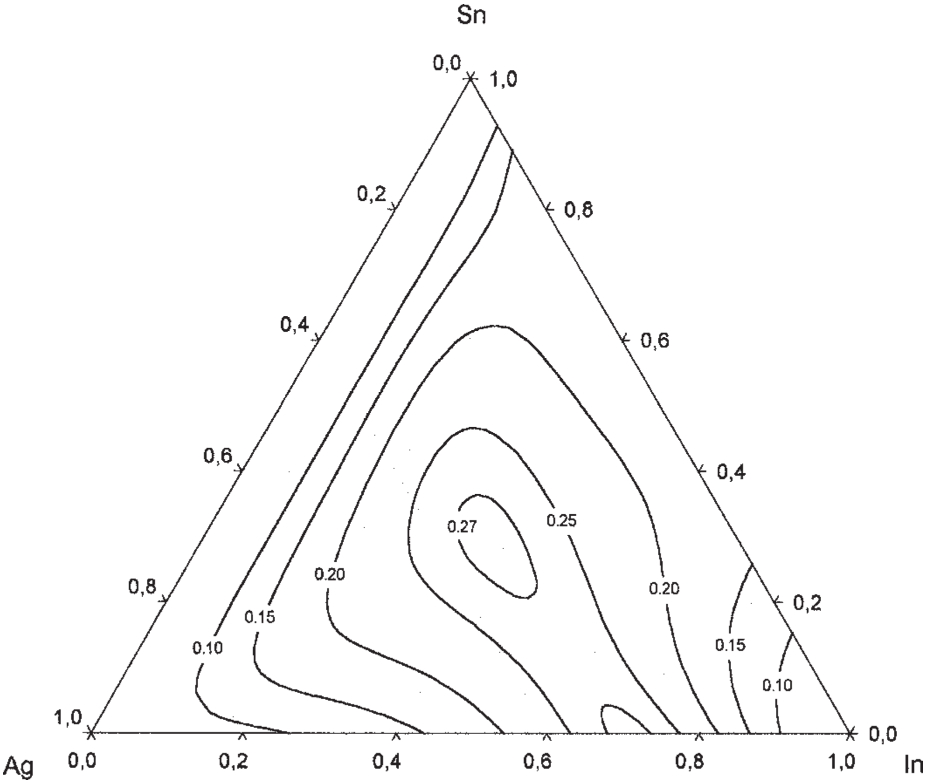

Figure 4. Concentration–concentration fluctuations $S_{cc}^{InIn}(0)$ in liquid Ag–In–Sn at 973 K.

the thermodynamic resistance against complete separation of the constituents. The interactions between the constituent atoms (introduced in real systems via H^{m} and S^{xs}, and therewith via G^{xs}) give only rise to additional effects. In order to work out some of the interesting details the discussion will be continued with 'excess quantities', i.e. the departures from the ideal behaviour

$$\begin{aligned} \Delta S_{cc}^{ij}(0) &= S_{cc}^{ij}(0) - S_{cc}^{ij,\,id}(0) \\ \Delta\sigma &= \sigma - \sigma^{id} \\ \Delta c_i^{m} &= c_i^{m} - c_i^{m,\,id} \end{aligned} \tag{11}$$

Special emphasis will be given to the section with $c_{In}/c_{Sn} = 1$. The most important numerical results are listed in table 1. Figure 6a–c summarize the variation of all quantities under consideration with increasing Ag-content along this particular section. The most remarkable variations are those of $S_{cc}^{AgAg}(0)$ and $\Delta\sigma$. Obviously, it is primarily the surplus amount of Ag-atoms on the surface (Δc_{Ag}^{m}) which determines whether the surface tension is higher or lower than the ideal value. The increase of $S_{cc}^{AgAg}(0)$ over the ideal value in alloys rich in In or Sn ($\Delta S_{cc}^{AgAg}(0)) > 0$ for $c_{Ag} < 0.5$) leads to the slightly increased segregation of Ag-atoms from the surface into the bulk ($\Delta c_{Ag}^{m} < 0$)

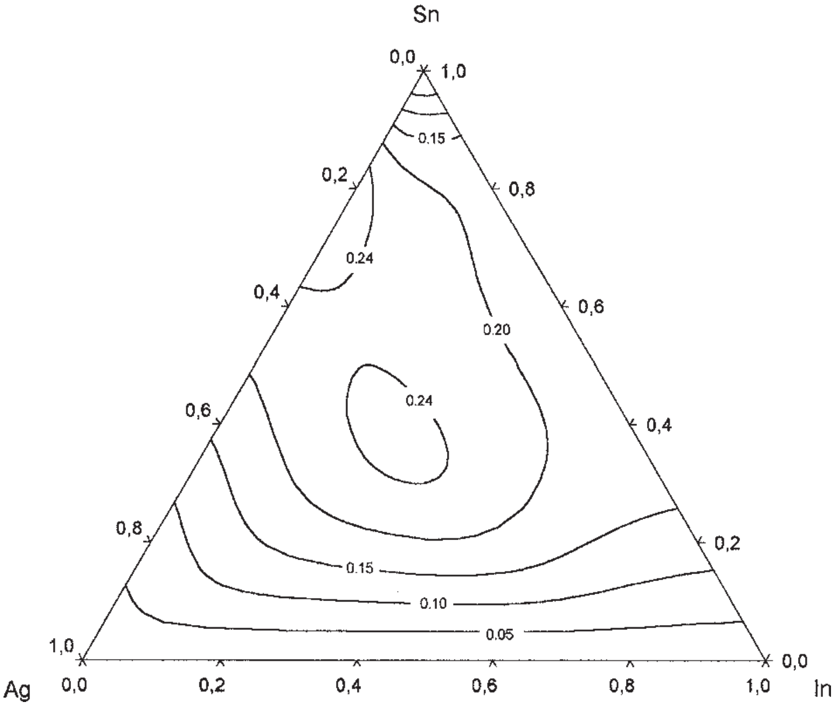

Figure 5. Concentration–concentration fluctuations $S_{cc}^{SnSn}(0)$ in liquid Ag–In–Sn at 973 K.

Table 1. Surface concentrations ($c_{Ag}^{m}, c_{In}^{m}, c_{Sn}^{m}$), surface tension ($\sigma$), and viscosity ($\eta$) of liquid Ag–In–Sn in the section with $c_{In}/c_{Sn} = 1$ at 973 K.

c_{Ag}	c_{Ag}^{m}	c_{In}^{m}	c_{Sn}^{m}	σ (mN m^{-1})	η (mPa s)
0	0	0.510	0.490	0.517	0.7775
0.1	0.005	0.499	0.496	0.526	0.8659
0.2	0.009	0.495	0.496	0.535	1.0474
0.3	0.013	0.491	0.496	0.542	1.2649
0.4	0.016	0.488	0.496	0.552	1.5048
0.5	0.021	0.480	0.496	0.566	1.7642
0.6	0.029	0.466	0.505	0.590	2.0568
0.7	0.049	0.445	0.506	0.634	2.4273
0.8	0.106	0.403	0.491	0.708	2.9829
0.9	0.360	0.260	0.380	0.824	3.9938
1	1	0	0	1.016	6.5768

and conversely (always with respect to the ideal case) to the increased abundance of In-atoms on the surface ($\Delta c_{In}^{m} > 0$) which gives rise to a low surface tension ($\Delta\sigma < 0$ for $c_{Ag} < 0.5$). On an absolute scale, the actual concentration of Sn-atoms in the surface layer is in general even slightly higher than that of In (see values given in table 1) due to the thermodynamics of the system, $\Delta c_{Sn}^{m} < 0$ means only that their concentration is below that of the ideal mixture.

On the other hand, the decrease of $S_{cc}^{AgAg}(0)$ indicated for alloys with high contents of Ag (i.e. $\Delta S_{cc}^{AgAg}(0) < 0$ for $c_{Ag} > 0.5$) points to a recovered tendency of Ag-atoms to stay on the surface which would suggest an increase in surface tension. This, however,

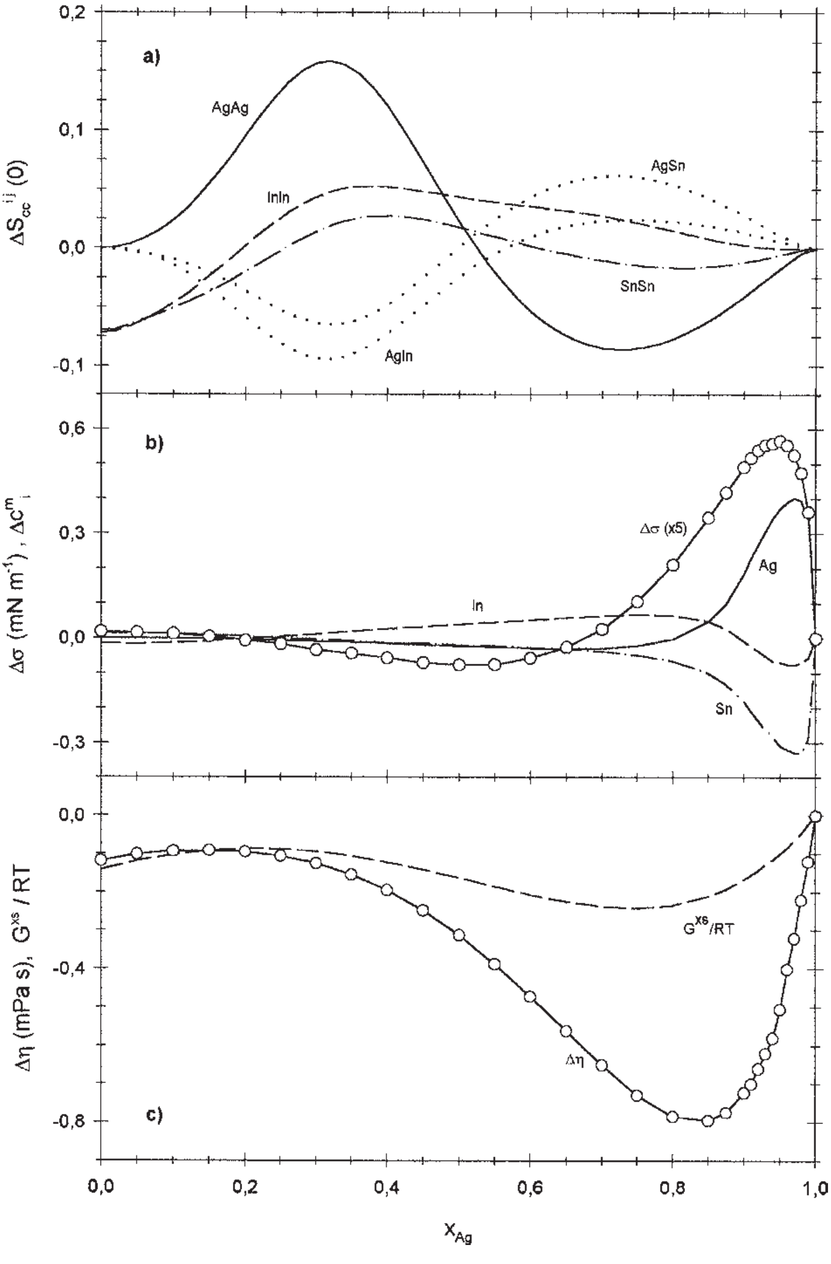

Figure 6. Deviations of selected physical properties from the ideal behaviour in liquid Ag–In–Sn along the section $c_{\mathrm{In}}/c_{\mathrm{Sn}} = 1$ at 973 K. (a) Concentration–concentration fluctuations $\Delta S_{\mathrm{cc}}^{ij}(0)$, (b) surface tension $\Delta\sigma$ and surface concentrations Δc_i^{m} and (c) viscosity $\Delta\eta$ and excess free energy of mixing G^{xs}/RT.

is counteracted by the positive deviation of $S_{\mathrm{cc}}^{\mathrm{InIn}}(0)$ from the ideal value which signals that on behalf of a low surface energy In-atoms still tend to be attracted into the surface layer, provided the concentration in Ag is not too high. As a result, on further increasing c_{Ag} the surface concentrations and the additional surface tension itself

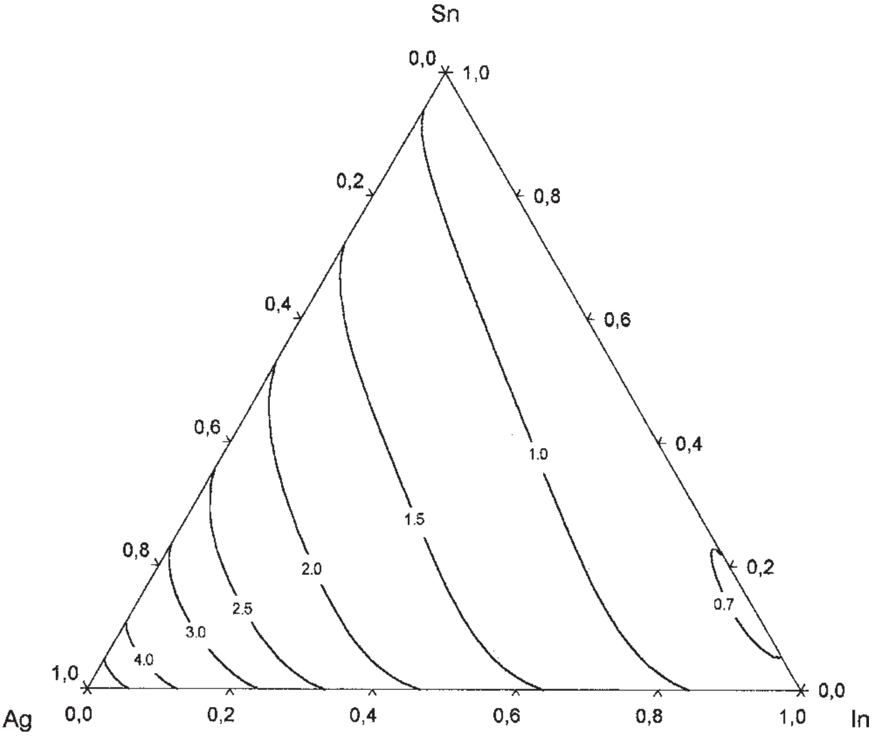

Figure 7. Viscosity in liquid Ag–In–Sn at 973 K.

show retarded cusp-like deviations from the values predicted for the ideal behaviour (figure 6b). Strictly, the influence of $S_{cc}^{SnSn}(0)$ goes parallel to that of $S_{cc}^{InIn}(0)$, but since $\Delta S_{cc}^{SnSn}(0) < \Delta S_{cc}^{InIn}(0)$ its influence on the distribution of the atoms on the surface is less pronounced.

It is interesting to note that – in coincidence with the appearance of the crystalline ζ-phase [4] – the maximum of $\Delta S_{cc}^{AgSn}(0)$ around $c_{Ag} \approx 0.7$ hints at a preferential heterocoordination which would definitely act against the separation of Ag and Sn. Such a preference of unlike neighbours is less pronounced in $S_{cc}^{AgIn}(0)$. Together with the higher values of $S_{cc}^{InIn}(0)$ this underlines why in this particular range of composition Sn-atoms are less attracted to the surface than In-atoms.

The variation of the viscosity across the entire ternary system is shown in figure 7. The results obtained for the section $c_{In}/c_{Sn} = 1$ are listed in table 1. Over a wide range of composition the viscosity adopts values not essentially higher than those of pure In ($\eta_{In} = 0.77$ mPa s) or Sn ($\eta_{Sn} = 0.93$ mPa s). Up to $c_{Ag} \approx 0.6$ the increase due to the addition of Ag is moderate (table 1), followed by a rapid increase towards the value of pure Ag extrapolated to the reference temperature ($\eta_{Ag} = 6.58$ mPa s). The deviations from the ideal value ($\Delta\eta = \eta - \eta^{id}$) pass through a deep minimum located around $c_{Ag} \approx 0.8$ which is also near to the composition where the minimum in G^{xs} (figure 6c) and the formation of the ζ-phase occur [4]. It is obvious that concerning the variation with the composition $\Delta\eta$ and G^{xs} follow the same trend. This is due to the fact, that according to equation (7) the free energy of activation G^* is reduced from the ideal value due to the negative contribution of G^{xs} to G^m.

The experimental results reported for In–Sn [9] do not confirm the shallow minimum indicated on the In–Sn side of the system (figure 7). However, the scatter of the experimental data points ($\pm 0.2\,\mathrm{mPa\,s}$) is probably too large to reveal such small effects.

In conclusion, it must be recalled that discussion was concerned with the deviations of the quantities from the ideal value, thus the considerations refer only to the trend superimposed on the behaviour of an ideal system which neglects the interactions of the system. Therefore, the conclusions given in terms of the excess quantities reflect only the additional trends originating from the interactions between the atoms. Moreover, the interpretation was mainly focused on $S_{\mathrm{cc}}^{\mathrm{AgAg}}(0)$ since it showed the most marked deviations from ideality, but strictly the findings are the result of the interplay of all structure factors.

As regards the various models of the viscosity cited in literature, it has to be mentioned that most of them employ the heat of mixing as measure of the atomic interaction [23]. Consequently, the deviations of the viscosity from the ideal mixing behaviour will always be determined by the sign of the heat of mixing which leads to conflicting results in the case of Ag–In and Ag–Sn. Seetharaman and Du Sichen [6] were successful in explaining the experimental viscosity of these systems by using a more elaborate formalism based on the free energy of mixing. Therefore, their model was also used to give a first idea of the viscosity in the ternary system Ag–In–Sn.

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