Int J Thermophys (2009) 30:1811–1822
DOI 10.1007/s10765-009-0663-6

Thermophysical Properties of Liquid In–Sn Alloys

**Z. Moser · W. Gąsior · J. Pstruś ·
I. Kaban · W. Hoyer**

Received: 30 March 2009 / Accepted: 7 October 2009 / Published online: 24 October 2009

Abstract The surface tension of liquid In–Sn alloys was measured with three experimental techniques carried out in a protective atmosphere of a mixture of argon and hydrogen: tensiometric (in Chemnitz), and maximum bubble pressure and sessile drop (in Kraków). Attempts were undertaken to confirm the correlation of surface tension with electrical conductivity and viscosity and to compare them with literature data. The lack of such correlation or a weak one was observed, probably due to a slight negative departure of thermodynamic properties of liquid In–Sn alloys from ideal behavior. Both resistivity and viscosity correlated with the existence of In-rich β and Sn-rich γ phases of the In–Sn phase diagram. The mutual correlations of thermodynamic and physical properties, structure, and the type of phase diagram were confirmed previously for Li–Sn and Mg–Sn systems with evident negative thermodynamic departures from ideal behavior and with the occurrence of intermetallic compounds (IMCs) in the phase diagrams. Due to nearly the same values of surface tension and density of pure In and Sn, the concentration dependence on the surface tension and density was practically unchanged within an extensive range of temperatures in studies on Pb-free solders of binary and multicomponent alloys containing both metals. Thus, the beneficial influence of In on the wettability of In–Sn alloys was observed solely by the lowering of the contact angle.

Keywords Electrical conductivity · Surface tension · Various correlations · Viscosity

---

Z. Moser (✉) · W. Gąsior · J. Pstruś
Institute of Metallurgy and Materials Science, Polish Academy of Sciences, 25, Reymonta Street,
30-059 Kraków, Poland
e-mail: nmmoser@imim-pan.krakow.pl

I. Kaban · W. Hoyer
Institute of Physics, Chemnitz University of Technology, 09107 Chemnitz, Germany

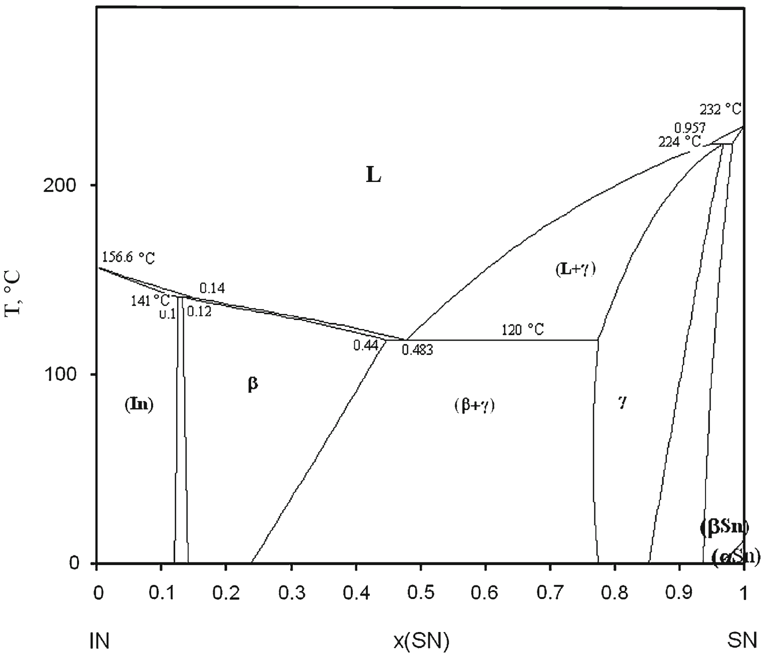


Fig. 1 Phase diagram of the In–Sn system calculated using thermodynamic data presented by Lee et al. [1]

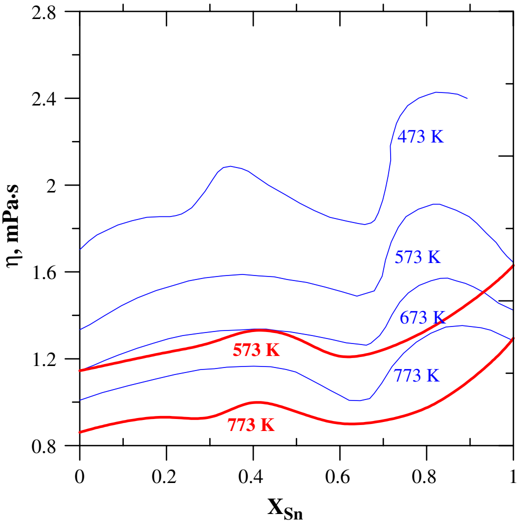
1 Introduction

The In–Sn alloys exhibit slightly negative deviations of enthalpy and Gibbs energy of mixing from ideal behavior, and the phase diagram is characterized by wide ranges of the In-rich β-phase and the Sn-rich γ phases as shown, for example, by Lee et al. [1]. Orr et al. [2] observed a considerable decrease of the heat capacity, C_P, with increasing temperature at 0.4722 mole fraction of Sn (394 K to 758 K). They interpreted it as a result of a decrease of interactions of non-random associations between different atoms, resulting in positive ΔC_P and possible changes in the liquid structure of In–Sn alloys.

The suggestions of Orr et al. [2] were supported by extremes in viscosity reported by Walsdorfer et al. [3] and confirmed recently by Gruner and Hoyer [4]. The phase diagram by Lee et al. [1] is presented in Fig. 1, and the viscosity isotherms from Refs. [3] and [4] are shown in Fig. 2.

The viscosity at different temperatures as a function of composition, presented in Fig. 2, increased above the normal value in the region where two intermetallic compounds (IMCs) in the In-rich β and Sn-rich γ phases were present. At lower temperatures (473 K) these maxima were more evident, while at higher temperatures they became weaker due to a reduction of short-range interactions. The viscosity isotherms at higher temperatures, reported in Refs. [3] and [4], revealed the minima above 0.6 mole fraction of Sn. A similar anomaly in the electrical conductivity at alloy compositions of 0.46 and 0.90 mole fractions of Sn was observed by Predel and Sandig [5]

Fig. 2 Viscosity isotherms of Walsdorfer et al. [3] (*thin lines*) and Gruner and Hoyer [4] (*thick lines*) as a function of Sn content



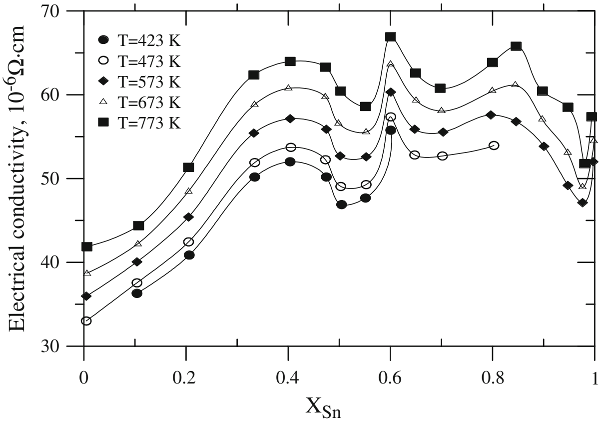


Fig. 3 Isothermal electrical conductivity of In–Sn liquid alloys presented by Predel and Sandig [5]

as is presented in Fig. 3. Additionally, a considerable increase of electrical conductivity was also noted at 0.60 mole fraction of Sn, at which a decrease of viscosity was previously observed.

This study is focused on an analysis of the reported data for the viscosity and electrical conductivity of liquid In–Sn alloys, along with previously published data for the surface tension together with the new data obtained in Chemnitz and Krakow which were discussed and presented during a recent Thermodynamics of Alloys (TOFA) conference in Kraków [6]. The previous data for the surface tension of liquid In–Sn alloys are plotted in Fig. 4, indicating a slight deviation from ideal behavior observed at 773 K. These deviations were, to some extent, within the experimental error. Only Liu et al. [7] reported maxima of the surface tension in the γ-phase region in alloys with higher concentrations of tin.

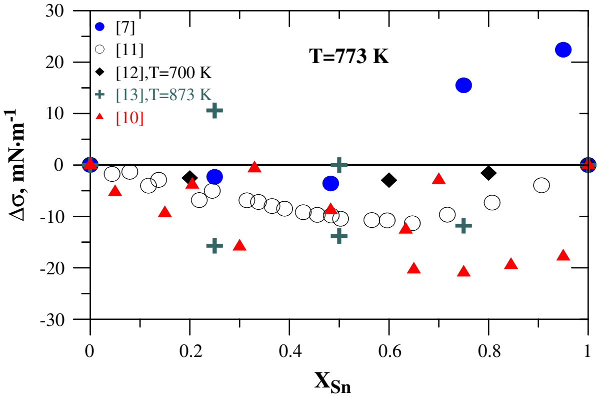


Fig. 4 Deviations of the surface tension from additivity of liquid In–Sn alloys reported by Liu et al. [7], Novakovic et al. [10], Dadashev et al. [11], Kononenko et al. [12], and Tanaka et al. [13]

It should be noted that correlations of thermodynamic properties with physical properties, the structure of liquid alloys, and the type of the phase diagram were observed previously in the Li–Sn [8] and Mg–Sn [9] systems, which are characterized by evident negative enthalpy and Gibbs energy of mixing and the formation of the strong IMCs.

2 Experimental and Modeled Surface Tension and Density Data Based on Maximum Bubble Pressure, Sessile Drop, and Tensiometric Methods

The surface tension data of Liu et al. [7] shown in Fig. 4 with maximum values at about $X_{\mathrm{Sn}} = 0.8$ were repeated by Pstruś [14] for the following compositions: $X_{\mathrm{In}} = 0.875, 0.75, 0.65, 0.517, 0.4, 0.25, 0.2, 0.10$, and 0.05 with two experimental techniques: maximum bubble pressure (m.b.) and sessile drop (s.d.) over wide temperature ranges.

The tensiometric method (t.m.) was applied also to the surface tension measurements at Chemnitz. In each method, a protective atmosphere of argon with 10 % hydrogen was used. The density required for the surface tension calculations was measured in Krakow separately by the dilatometric technique, while in Chemnitz simultaneously with the surface tension. The details of the experimental techniques for surface tension and density measurements reported in [14] are presented in the SURDAT database of Pb-free soldering materials [15], while those performed by the t.m. were reported in [16]. The experiments were performed in a vertical chamber, which was evacuated to less than 5×10^{-5} mbar and then filled with a gas mixture of Ar-10 % H_2 (∼1 bar) before heating [16]. The experimental uncertainty did not exceed 3 % for the surface tension and 1.5 % for the density measurements. All In–Sn alloys were prepared from pure Sn and In (both 99.999 mass%). A gas mixture of argon with hydrogen acts against oxidation and therefore is more convenient than vacuum as formation of oxides influences the precision of the surface tension measurements.

Table 1 Temperature dependencies of the surface tension of the In–Sn liquid alloys measured by the tensiometric method together with the least-squares linear equations $\sigma = a + bT$ ($\text{mN} \cdot \text{m}^{-1}$), calculated errors of a and b coefficients, and calculated values of the surface tension at $T = 523$ K and 773 K

X_{In}	a ($\text{mN} \cdot \text{m}^{-1}$)	b ($\text{mN} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)	σ_{523} K ($\text{mN} \cdot \text{m}^{-1}$)	σ_{773} K ($\text{mN} \cdot \text{m}^{-1}$)	Err(a) ($\text{mN} \cdot \text{m}^{-1}$)	Err(b) ($\text{mN} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)
1.0	593.1	−0.1013	540.1	514.8	±1.4	±0.0020
0.9	603.4	−0.1167	542.4	513.2	±2.2	±0.0029
0.8	577.5	−0.0945	528.1	504.5	±2.1	±0.0026
0.7	583.2	−0.1062	527.7	501.1	±2.6	±0.0033
0.6	571.4	−0.0885	525.1	503.0	±2.3	±0.0028
0.5	581.8	−0.0957	531.7	507.8	±2.1	±0.0027
0.4	586.3	−0.1043	531.8	505.7	±2.9	±0.0036
0.2	587.3	−0.1029	533.5	507.8	±2.8	±0.0033
0	582.7	−0.0940	533.5	510.0	±3.7	±0.0047

Table 2 Temperature dependencies of the density of the In–Sn liquid alloys obtained using the tensiometric method together with the least-squares linear equations $\rho = a + bT$ ($\text{g} \cdot \text{cm}^{-3}$) errors of a and b parameters, and the densities and their errors calculated at 523 K

X_{In}	a ($\text{g} \cdot \text{cm}^{-3}$)	b ($\text{g} \cdot \text{cm}^{-3} \cdot \text{K}^{-1}$)	ρ_{523} K ($\text{g} \cdot \text{cm}^{-3}$)	Err(a) ($\text{g} \cdot \text{cm}^{-3}$)	Err(b) ($\text{g} \cdot \text{cm}^{-3} \cdot \text{K}^{-1}$)
1	7.2475	−0.00061	6.928	±0.026	±0.000032
0.9	7.2182	−0.00056	6.925	±0.008	±0.000013
0.8	7.3903	−0.00073	7.009	±0.011	±0.000014
0.7	7.2238	−0.00060	6.910	±0.046	±0.000058
0.6	7.2229	−0.00056	6.930	±0.010	±0.000012
0.5	7.2358	−0.00058	6.932	±0.018	±0.000022
0.4	7.1668	−0.00050	6.905	±0.021	±0.000028
0.2	7.2596	−0.00060	6.946	±0.007	±0.000011
0	7.2422	−0.00062	6.918	±0.043	±0.000054

Results of surface tension and density by t.m. are presented in Tables 1 and 2, respectively.

The surface tension data obtained by the m.b. pressure and s.d. methods are presented in Tables 3 and 4, respectively, while the density results from dilatometric measurements from Krakow are reported in Table 5.

Using experimental data from Tables 1, 3, and 4, isotherms of the surface tension were calculated and presented in Fig. 5. Some minima in the range of the β phase in the In–Sn phase diagram are visible in Fig. 5. No fluctuations are observed in the surface tension curves calculated by Butler's method [17] using thermodynamic functions evaluated by Lee et al. [1].

Comparisons of results on surface tension from Chemnitz and Kraków are presented in Figs. 6 and 7 at 532 K and 973 K, respectively.

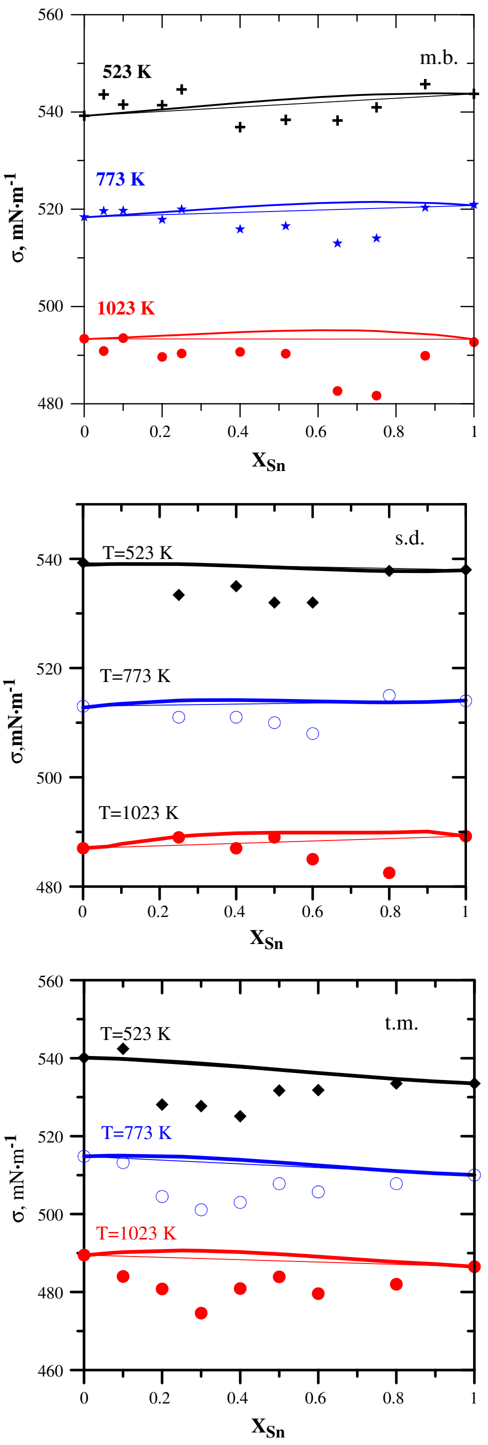


Fig. 5 Surface tension isotherms of the In–Sn liquid alloys obtained using different methods (m.b., s.d., and t.m.) together with these calculated by Butler model [17] (indicated as curvilinear dependence) using the thermodynamic parameters from [1] and the pure component data obtained in this article

Table 3 Temperature dependencies of the surface tension of the liquid In–Sn alloys measured by the maximum-bubble-pressure method together with the least-squares linear equations $\sigma = a + bT\,(\mathrm{mN \cdot m^{-1}})$ and calculated errors of a and b coefficients and the surface tension at $T = 523$ K and $T = 773$ K

X_{In}	a $(\mathrm{mN \cdot m^{-1}})$	b $(\mathrm{mN \cdot m^{-1} \cdot K^{-1}})$	σ_{523} K $(\mathrm{mN \cdot m^{-1}})$	σ_{773} K $(\mathrm{mN \cdot m^{-1}})$	Err(a) $(\mathrm{mN \cdot m^{-1}})$	Err(b) $(\mathrm{mN \cdot m^{-1} \cdot K^{-1}})$
1.000	595.2	−0.0949	545 ± 9	522 ± 9	±9.4	±0.0114
0.875	603.4	−0.1060	548 ± 5	522 ± 4	±6.9	±0.0075
0.750	594.9	−0.1042	540 ± 7	514 ± 7	±8.1	±0.0085
0.650	590.3	−0.0997	538 ± 5	513 ± 7	±6.5	±0.0075
0.517	584.1	−0.0874	538 ± 5	517 ± 5	±6.5	±0.0075
0.400	577.3	−0.0804	535± 7	515 ± 7	±6.7	±0.0085
0.250	595.3	−0.0973	544 ± 8	520 ± 8	±6.2	±0.0074
0.200	583.6	−0.0849	539 ± 7	518 ± 6	±6.7	±0.0076
0.100	585.4	−0.0854	541 ± 7	519 ± 6	±7.1	±0.0087
0.050	591.3	−0.0934	543 ± 6	519 ± 6	±7.3	±0.0088
0.000	582.8	−0.0834	538 ± 9	518± 9	±6.3	±0.0075

Table 4 Temperature dependencies of the surface tension of the liquid In–Sn alloys measured by the sessile drop method together with the least-squares linear equations $\sigma = a + bT\,(\mathrm{mN \cdot m^{-1}})$ and calculated errors of a and b coefficients and the surface tension at $T = 523$ K and $T = 773$ K

X_{In}	a $(\mathrm{mN \cdot m^{-1}})$	b $(\mathrm{mN \cdot m^{-1} \cdot K^{-1}})$	σ_{523} K $(\mathrm{mN \cdot m^{-1}})$	σ_{773} K $(\mathrm{mN \cdot m^{-1}})$	Err(a) $(\mathrm{mN \cdot m^{-1}})$	Err(b) $(\mathrm{mN \cdot m^{-1} \cdot K^{-1}})$
1.000	593.8	−0.0942	545 ± 12	521 ± 11	±11.9	±0.0144
0.875	598.8	−0.1015	546 ± 7	520 ± 6	±9.3	±0.0103
0.750	597.3	−0.1077	541 ± 10	514 ± 9	±10.7	±0.0116
0.650	591.1	−0.1011	538 ± 9	513 ± 8	±9.1	±0.0103
0.517	584.1	−0.0874	538 ± 5	517 ± 5	±6.5	±0.0075
0.400	580.8	−0.0914	537 ± 10	516 ± 10	±9.0	±0.0117
0.250	596.3	−0.0987	545 ± 9	520 ± 8	±6.2	±0.0074
0.200	590.6	−0.0941	541 ± 6	518 ± 7	±3.2	±0.0061
0.100	587.2	−0.0873	542 ± 7	520 ± 7	±5.4	±0.0097
0.050	593.8	−0.0959	544 ± 6	520 ± 5	±6.5	±0.0114
0.000	582.8	−0.0834	539 ± 10	518 ± 9	±6.6	±0.0079

The analysis of density isotherms shown in Tables 2 and 5 suggested lack of correlation with surface tension results (Fig. 5).

3 Discussion

The results of surface tension measurements carried out in Chemnitz and Kraków presented in Fig. 5 showed some similarities between the results of m.b. and t.m. experiments. In both the techniques, the surface of the measured alloy was renewed—in the

Table 5 Temperature dependencies of the density of the In–Sn liquid alloys obtained using the tensiometric method together with the least-squares linear equations $\rho = a + bT\,(\mathrm{g \cdot cm^{-3}})$ errors of a and b parameters, and the densities and their errors calculated at 523 K

X_{In}	a $(\mathrm{g \cdot cm^{-3}})$	b $(\mathrm{g \cdot cm^{-3} \cdot K^{-1}})$	ρ_{523} K $(\mathrm{g \cdot cm^{-3}})$	Err(a) $(\mathrm{g \cdot cm^{-3}})$	Err(b) $(\mathrm{g \cdot cm^{-3} \cdot K^{-1}})$
1.000	7.3206	−0.000684	6.963 ±0.027	±0.02	±0.000039
0.875	7.3170	−0.000660	6.972 ±0.076	±0.069	±0.000114
0.750	7.3221	−0.000710	6.951 ±0.052	±0.048	±0.000081
0.650	7.2753	−0.000661	6.930 ±0.095	±0.112	±0.000128
0.517	7.2332	−0.000599	6.920 ±0.025	±0.022	±0.000038
0.400	7.2540	−0.000602	6.939 ±0.023	±0.033	±0.000036
0.250	7.2983	−0.000619	6.975 ±0.035	±0.031	±0.000051
0.200	7.2668	−0.000616	6.944 ±0.029	±0.024	±0.000045
0.100	7.2240	−0.000573	6.924 ±0.024	±0.019	±0.000035
0.050	7.3338	−0.000654	6.992 ±0.032	±0.029	±0.000053
0.000	7.3801	−0.000681	7.024 ±0.027	±0.034	±0.000037

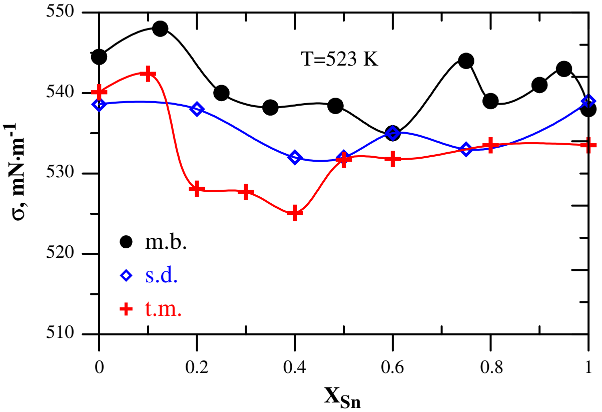


Fig. 6 Comparison of the results of surface tension experiments of liquid In–Sn alloys carried out in Chemnitz (t.m.) and Kraków (m.b. and s.d.) at 523 K

m.b. method by bubbling the protective gas (argon + hydrogen) through the melt, and in the t.m. experiment by moving the alumina stamp submerged below the level of the free liquid surface. In the s.d. technique, a drop rests on the substrate and requires a special atmosphere to protect its surface. Therefore, the protective atmosphere is extremely important in the s.d. experiment. To decrease that effect, Novakovic et al. [10] used a large drop method and performed the measurements under a vacuum of 10^{-4} Pa and very low oxygen content. Even so, their results were scattered as shown in Fig. 8, in which most of their surface tension data at 773 K are collected.

Contrary to most surface tension data for pure components, the results of Ref. [10] for Sn were higher than for In, which means that In atoms segregated to the surface over the complete concentration and temperature ranges examined. The opposite case

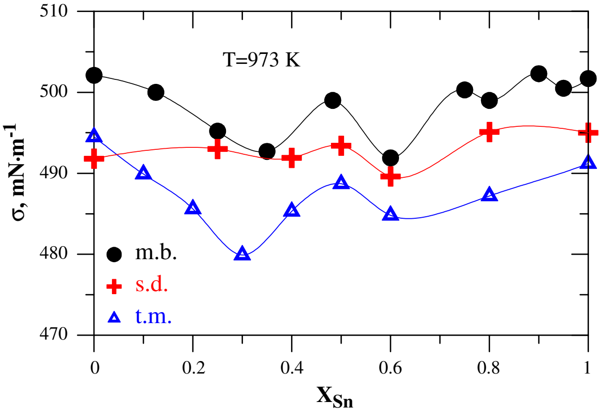


Fig. 7 Comparison of the results from surface tension measurements of liquid In–Sn alloys carried out at 973 K in Chemnitz (t.m.) and Kraków (m.b. and s.d.)

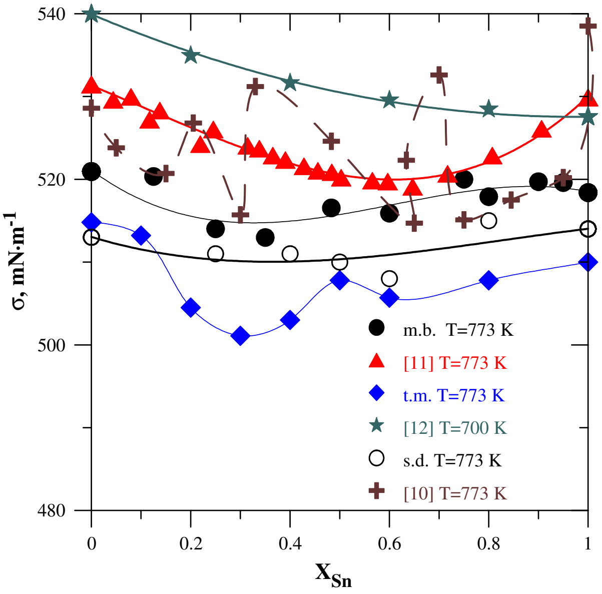


Fig. 8 Isotherms of surface tension of liquid Sn–In alloys obtained in the m.b. and s.d. experiments performed in Kraków and in the t.m. experiments carried out in Chemnitz, along with previously published data including also the results from Ref. [10]

was observed for the surface tension calculated based on the m.b. experiment. Taking into account the results plotted in Figs. 4 and 8, it would be difficult to find similarities between the presented data, most exhibiting a negative deviation from ideal behavior and oscillating around the values of surface tension of pure In and Sn. It is interesting to note that due to nearly the same surface tension and density of pure In and Sn, not only in liquid In–Sn and Ag–In-Sn [7] alloys, but also in Sn–Ag–Cu–In [18]

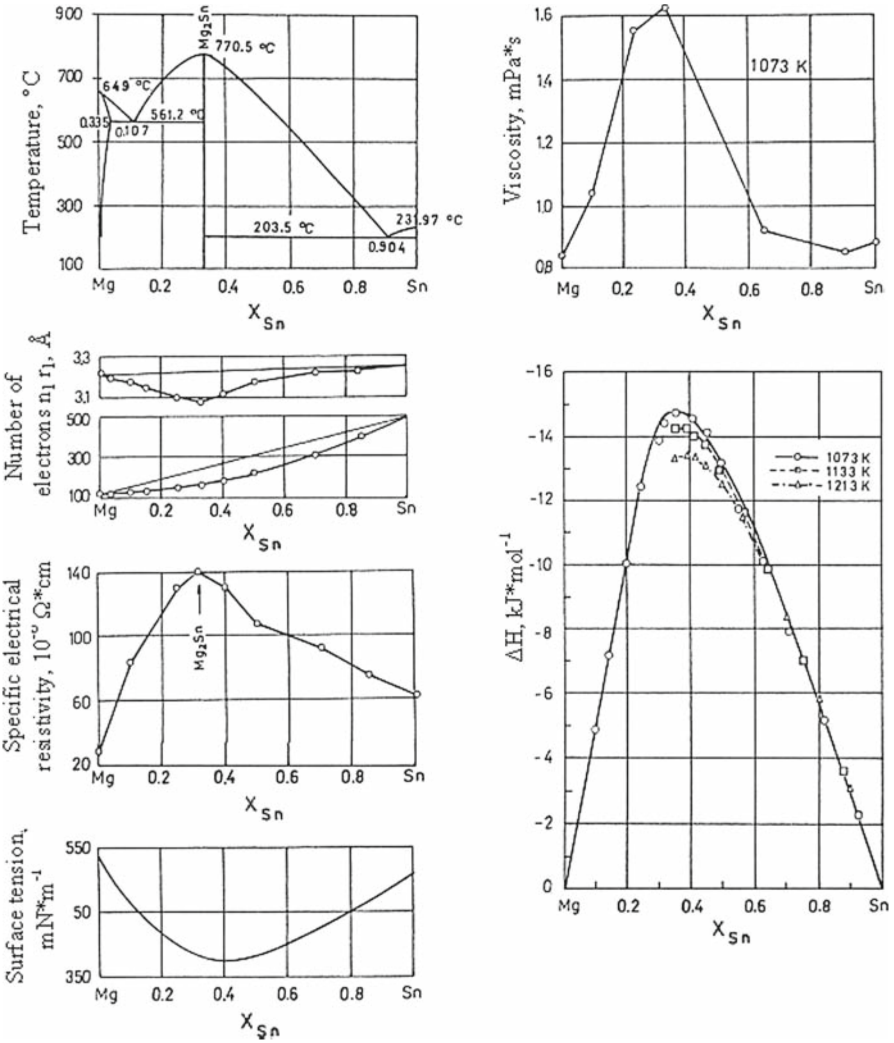


Fig. 9 Physical, structural, and thermodynamic properties of liquid Mg–Sn alloys reported in Ref. [9]. Starting from the *top* of the *left side*: phase diagram, atomic radius of the first coordination shell and distribution curve in the first coordination shell, specific electrical resistivity, surface tension, viscosity, and enthalpy of mixing

and Sn–Zn–In [14] alloys, the concentration dependence of the surface tension and density over a wide range of temperatures is practically the same, and the beneficial influence on wettability with the addition of In in these alloys was observed solely by the decrease of the contact-angle values.

No correlation or a weak correlation observed for the surface tension should be discussed from the point of view of previously presented anomalies in viscosity [3,4] and electrical conductivity [5] in the In–Sn alloys exhibiting slight negative deviations of the enthalpy and Gibbs energy of mixing from ideal behavior [1].

Such correlations were observed in systems with evident negative deviations of thermodynamic properties and the existence of IMCs in the phase diagram. To follow these suggestions, various properties of Mg–Sn alloys, which exhibit extreme values corresponding to the existence of the Mg_2Sn compound in the phase diagram were plotted in Fig. 9 based on Ref. [9]. For the case of the enthalpy of mixing, the experimentally obtained dependence on temperature is indicated by the maximum values at the lowest temperature, at which the influence of the short-range interactions (connected with the existence of associates) is the most visible. It is evident that the maximum values of viscosity and specific electrical resistivity are followed by minimum values of surface tension. Such typical correlations were not observed in the case of liquid In–Sn alloys, but the structural phenomena are probably responsible for the observed behavior. For the case of Mg–Sn alloys [9], the minimum is observed at the atomic radius of the first coordination shell with a continuous change in the electron distribution curve in the same coordination shell.

Liquid In–Sn alloys were examined also with neutron and X-ray diffraction experiments on a specimen of the In–Sn 80 alloy by Zu et al. [19] and by Kaban et al. [20], who revealed the effect of temperature on structure. Results of those studies taking into account interatomic distance r_1 and coordination number N_1 are not consistent, and more advanced structure studies are recommended.

4 Conclusions

Mutual correlations of various properties observed in Li–Sn [8] and Mg–Sn [9] were not confirmed for In–Sn alloys probably due to their slight negative deviations from ideal thermodynamic behavior. It seems that the most probable reasons for the peculiar electrical conductivity and viscosity dependencies of the In–Sn alloys are connected with structural phenomena. It is interesting that no concentration dependence of the surface tension and density over a wide range of temperature has been observed not only in the In–Sn alloys but also in ternary and quaternary alloys containing indium and tin. It is due to nearly the same surface tension and density of pure In and Sn, and in the In–Sn alloys, as well as probably to the peculiar structure of In–Sn melts.

References

1. B.J. Lee, C.S. Oh, J.H. Shim, J. Electron. Mater. **25**, 983 (1996)
2. H. Orr, J. Giraud, R. Hultgren, Trans. ASM **55**, 853 (1962)
3. H. Walsdorfer, I. Apshofen, B. Predel, Z. Metallkd. **79**, 503 (1988)
4. S. Gruner, W. Hoyer, Midterm-Meeting of the COST-Action 531, Genova, Italy, 2006
5. B. Predel, H. Sandig, Mater. Sci. Eng. **6**, 110 (1970)
6. Z. Moser, W. Gąsior, J. Pstruś, I. Kaban, W. Hoyer, R. Novakovic, E. Ricci, D. Giurano, T. Lanata, Thermophysical properties of liquid In–Sn alloys, in *Proceedings of TOFA 2008*, Discussion Meeting on Thermodynamics of Alloys, Kraków 2008, Abstracts and Programs 30
7. X.J. Liu, Y. Inohana, I. Ohnuma, R. Kainuma, K. Ishida, Z. Moser, W. Gąsior, J. Pstruś, J. Electron. Mater. **31**, 1139 (2002)
8. W. Gąsior, Z. Moser, Arch. Metall. **44**, 83 (1999)
9. Z. Moser, K. Fitzner, Thermochim. Acta **332**, 1 (1999)
10. R. Novakovic, D. Giuranno, E. Ricci, T. Lanata, Surf. Sci. **602**, 1957 (2008)

11. R.Kh. Dadashev, Kh.I. Ibragimov, S. Yushaev, Iz. Vuz. Tsvet. Metall. **1**, 121 (1984)
12. V.I. Kononenko, S.P. Yatsenko, A.L. Sukhman, Russ. J. Phys. Chem. **46**, 911 (1972)
13. T. Tanaka, M. Matsuda, K. Nakao, Y. Katayama, D. Kaneko, S. Hara, X. Xing, Z. Qiao, Z. Metallkd. **92**, 1242 (2001)
14. J. Pstruś, Doctor's Thesis, Institute of Metallurgy and Materials Science, Polish Academy of Sciences, Kraków, 2007
15. Z. Moser, W. Gąsior, A. Dębski, J. Pstruś, *SURDAT Database of Lead-Free Soldering Materials*, Institute of Metallurgy and Materials, Polish Academy of Sciences, Kraków (2007), OREKOP, ISBN 83-60768-01-3
16. I. Kaban, S. Mhiaoui, W. Hoyer, J.-G. Gasser, J. Phys.: Condens. Mater. **17**, 7867 (2005)
17. J.A.V. Butler, Proc. R. Soc. London A, **CXXXV**, 348 (1932)
18. Z. Moser, P. Sebo, W. Gasior, P. Svec, J. Pstruś, Wettability studies of Sn–Ag–Cu–In liquid solders and interaction with Cu substrate, *in Proceedings of CALPHAD XXXVI*, The Pennsylvania State University, State College, PA, 2007, Program and Abstracts 35
19. F.-Q. Zu, X-F. Li, L-J. Guo, H. Yang, X.-B. Qin, Z.G. Zhu, Phys. Lett. A **324**, 472 (2004)
20. I. Kaban, S. Gruner, W. Hoyer, A. Il'inskii, A. Shpak, J. Non-Cryst. Solids **353**, 1979 (2007)