Density and Surface Tension of the Pb-Sn Liquid Alloys

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The maximum bubble pressure method and the dilatometric method were used, respectively, in measurements of surface tensions and densities of Pb-Sn liquid alloys. The experiments were carried out in the temperature range from 573 to 1200 K for the pure Pb, pure Sn, and 7 alloys of the compositions 0.1, 0.2, 0.26, 0.36, 0.5, 0.7, and 0.9 mole fraction of Pb. A straight-line dependence on temperature was observed and fitted by the method of least squares both for the densities and the surface tensions. The calculated density isotherm at 673 K showed a positive deviation from the linearity over the entire range of composition, and the same tendency was seen at 1173 K for compositions higher than $X_{Pb} = 0.26$. At the lower concentration of Pb, a nearly linear character of 1173 K isotherm was noted. In the case of surface tensions, both at the lowest and the highest temperatures (673 and 1173 K), the deviation from linearity with composition was negative, but deviation decreased with increasing temperature. The isotherms of the compositional dependence of surface tension calculated from the Butler model exhibit good agreement with experimental data.

1. Introduction

As pointed out by [1989Kle], the Romans used the Pb-Sn alloy for solder joinings of pipes. In the next centuries until today, Pb-Sn solder alloys have been widely used in the modern electronics industry because of their low melting points, good wettability, good corrosion resistance, low cost, and reasonable electrical conductivity. However, due to lead toxicity, the development of a new Pb-free solder that would replace the traditional Pb-Sn alloys has become a pressing need. In this respect, attempts have been undertaken to replace Pb with another component, which forms a eutectic with Sn similar to that of the Pb-Sn system and with similar surface tension. The equilibrium Pb-Sn system is characterized by a single eutectic reaction (26.1 at.% Pb) that occurs at 456 K [Massalski2].

The properties of each new soldering material are usually compared with Pb-Sn, and therefore, at the Institute of Metallurgy and Materials Science in Kraków, measurements of surface tension and density of liquid Pb-Sn alloys have been undertaken. On the other hand, surface tension data may be calculated from the assessed thermodynamic parameters of liquid Pb-Sn alloys by the Butler's model [1932But]. A comparison of experimental data with those obtained from modeling and with previous references is the main purpose of this study.

2. Experimental

The densities of liquid Pb-Sn liquid alloys were measured by a dilatometric method, which is based on measurements of the height of the liquid alloys in the crucible of known diameter at a series of fixed temperatures and calculated according to the relation

$$\rho = \frac{4m}{\pi d^2 h}\ (\mathrm{kg/m^3}) \qquad \text{(Eq 1)}$$

where ρ is the density, m is the mass of the metal or alloy in kilograms, d is the diameter of the crucible in meters, and h is the height of the metal or alloy in the crucible in meters.

The surface tension was determined by the maximum bubble pressure method and was based on the measurement of the pressure required to form and detach a bubble at the end of a capillary immersed in a melt at a known depth. Measurements were conducted at 3 to 4 depths with about 10 to 15 bubbles. In the first approximation, the value of surface tension was calculated using the following equation:

$$\sigma = \frac{rg}{2(h_m\rho_m - h_c\rho_c)}\ (\mathrm{N/m}) \qquad \text{(Eq 2)}$$

where r is the radius of the capillary in meters, g is the gravitational acceleration in m/s^2, h_m is the difference between the manometer liquid before and after immersion in the depth h_c in meters, and ρ_m and ρ_c are the densities of the manometric liquid and the alloy in kg/m^3, respectively.

More precise values of the surface tension were calculated using the Sugden method [1922Sug].

Pb of 99.995 at.% purity and Sn of 99.9995 at.% purity were used in the measurements of surface tensions and densities of the pure metals and in preparation of Pb-Sn alloys under a mixture of high-purity argon with hydrogen. The same gas was used in the maximum bubble pressure measurements and as a protection medium in the dilatometric measurements of density. The alloys were prepared in a furnace in which the experiments were also performed. Preparation was by melting proper amounts of metals in a graphite crucible, slowly mixing the liquid alloys by bubbling an Ar-H_2 mixture through the melt, and homogenizing for ~24 h.

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Table 1 Temperature dependencies of the density of Pb-Sn liquid alloys with the *a* and *b* parameter errors and the densities calculated at 873 K

X_{Pb}	$\rho = a + bT$ (g/cm^3)	$\rho_{(873K)}$ (g/cm^3)	Err(a) (g/cm^3)	Err(b) (g/cm^3)
1.0000*	11.4709 - 0.001318T	10.321	…	…
0.9000	11.1727 - 0.001170T	10.151 ± 0.066	±0.087	±0.000093
0.7000	10.3908 - 0.001022T	9.498 ± 0.132	±0.187	±0.000214
0.5000	9.8066 - 0.001152T	8.801 ± 0.071	±0.089	±0.000098
0.3500	9.1277 - 0.001161T	8.115 ± 0.091	±0.113	±0.000126
0.2610	8.8256 - 0.001121T	7.847 ± 0.042	±0.044	±0.000052
0.2000	8.4846 - 0.001049T	7.569 ± 0.069	±0.066	±0.000076
0.1000	7.9910 - 0.000893T	7.212 ± 0.022	±0.023	±0.000026
0.0000**	7.3120 - 0.000615T	6.775	…	…

*Data from [1983Smi]
**Data from [1977Kuc]

Table 2 Temperature dependencies of the surface tension of Pb-Sn liquid alloys with the *a* and *b* parameter errors and the surface tensions calculated at 973 K

X_{Pb}	$\gamma = a + bT$ (mN/m)	$\gamma_{(973K)}$ (mN/m)	Err(a) (mN/m)	Err(b) (mN/m)
1.000	=497.5 - 0.1096T	390.9 ± 4.6	±5.5	±0.0057
0.900	=510.3 - 0.1219T	391.7 ± 8.8	±11.7	±0.0124
0.700	=498.9 - 0.1041T	397.6 ± 6.9	±6.8	±0.0076
0.500	=489.8 - 0.0787T	413.3 ± 7.4	±11.3	±0.0122
0.350	=487.7 - 0.0559T	433.3 ± 3.3	±4.7	±0.0048
0.261	=505.1 - 0.0644T	442.5 ± 6.2	±9.0	±0.0096
0.200	=514.9 - 0.0628T	453.8 ± 2.8	±4.3	±0.0046
0.100	=542.8 - 0.0779T	467.0 ± 4.4	±7.4	±0.0079
0.000	=582.8 - 0.0834T	514.2 ± 9.2	±12.3	±0.0127

Each alloy was prepared separately and chemically analyzed after measurements.

3. Results and Discussion

The data for density and surface tension of each alloy showed linear dependences on temperature and were fitted by the least-squares method. The errors of the density at 873 K, the surface tension at 973 K, and *a* and *b* parameters of least-squares fits were estimated from the analysis of variance and are presented in Tables 1 and 2.

In Figure 1, the experimental results for densities are shown by points and the densities are calculated from the least-squares fits of Table 1 and are shown as continuous lines. The densities of tin and lead were taken from [1977Kuc] and [1983Bra].

A composite temperature-concentration dependence of the density of Pb-Sn liquid alloys was generated by the minimization method and can be expressed by the following relation:

$$\rho = \rho_{Pb}X_{Pb} + \rho_{Sn}X_{Sn} + (3.2666 - 0.00280042T)X_{Pb} + (-8.6124 + 0.0071354T)X_{Pb}^2 + (8.4775 - 0.0043350T)X_{Pb}^3 - 3.1318X_{Pb}^4 \text{ (g/cm}^3) \quad \text{(Eq 3)}$$

with the standard deviation equal to 0.030 g/cm^3. The isotherms of the density calculated at 573 and 1173 K are presented in Fig. 2 and are compared with the data of Tresh *et al.* [1968Thr] and with the data from this study calculated from equations summarized in Table 1 and from Eq 3. The

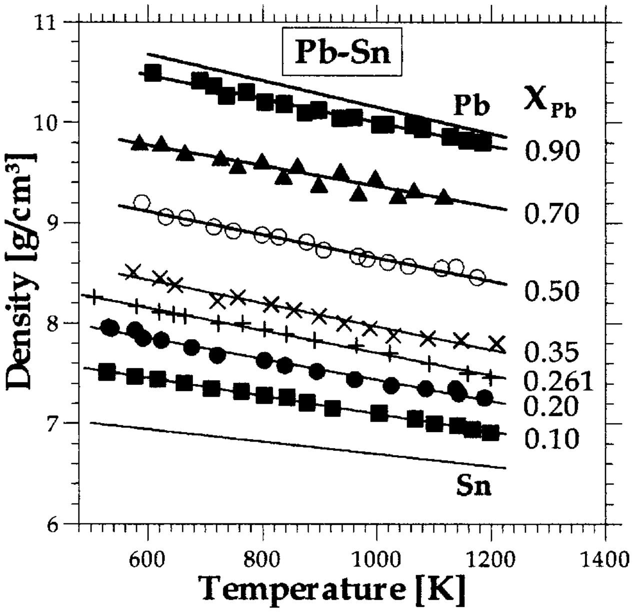

Fig. 1 Temperature dependencies of the density of Pb-Sn liquid alloys. Experimental results are shown as points, and straight lines present values calculated from the equation listed in Table 1

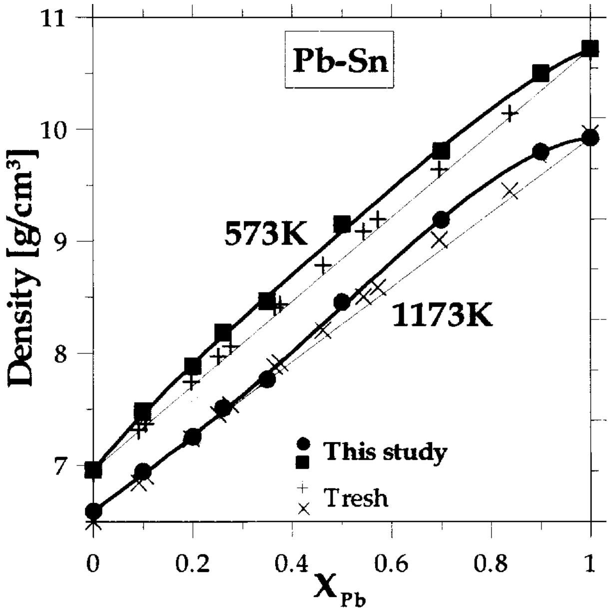

Fig. 2 Density isotherms of the Pb-Sn liquid alloys compared with data from the literature. Continuous lines are the values calculated from Eq 3. Full points are the data from this study calculated from equations presented in Table 1, and crosses are the data of [1968Tre]. Dotted lines are densities for unalloyed mixtures of Sn and Pb

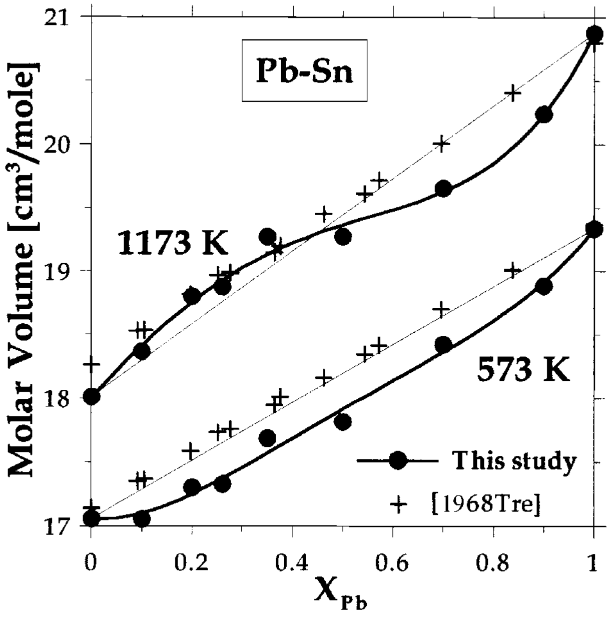

Fig. 3 Molar volume isotherms of Pb-Sn liquid alloys calculated from the data of this work and [1968Tre]. Continuous solid lines represent the molar volumes calculated from the densities of Pb-Sn liquid alloys described by Eq 3

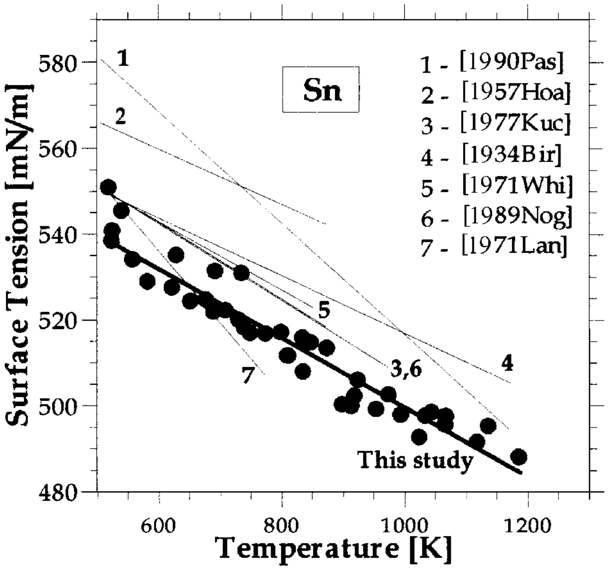

Fig. 4 Comparison of the surface tension of liquid tin obtained in this work with data from the literature

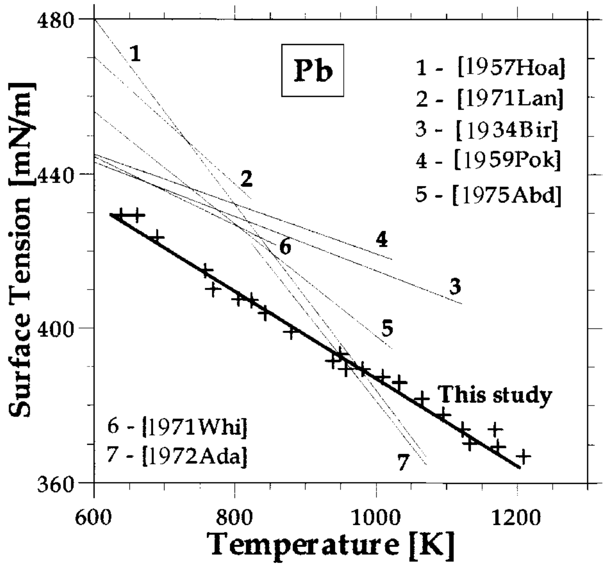

Fig. 5 Comparison of the surface tension of liquid lead obtained in this work with data from the literature

density isotherm at 573 K shows all values to be slightly higher than a linear interpolation between the pure Pb and the pure Sn values, while at 1173 K, the experimental values below the 0.7 mole fraction of the tin lie along a linear interpolation and only rise above the Sn-rich region. An inverse tendency is observed in the case of molar volume (Fig. 3). At 573 K, slight negative deviations from the ideal behavior are observed, and at higher temperature (1173 K), for compositions higher than 0.5 mole fraction of Pb. For 1173 K compositions below 0.5 mol.% Sn, deviations are positive. Because the density data of [1968Thr] in Fig. 2 exhibit only very slight positive deviations from linearity, nearly ideal changes of the molar volume in Fig. 3 are observed at both temperatures 573 and 1173 K.

The experimental results for the surface tension were evaluated in a manner analogous to the treatment of the density, and linear equations for tin, lead, and Pb-Sn alloys are listed in Table 2 together with the calculated errors and values of surface tension at 973 K. The surface tensions of tin, lead, and liquid Pb-Sn alloys are shown in Fig. 4, 5, and 6, respectively. The data for tin (Fig. 4) from the present study are

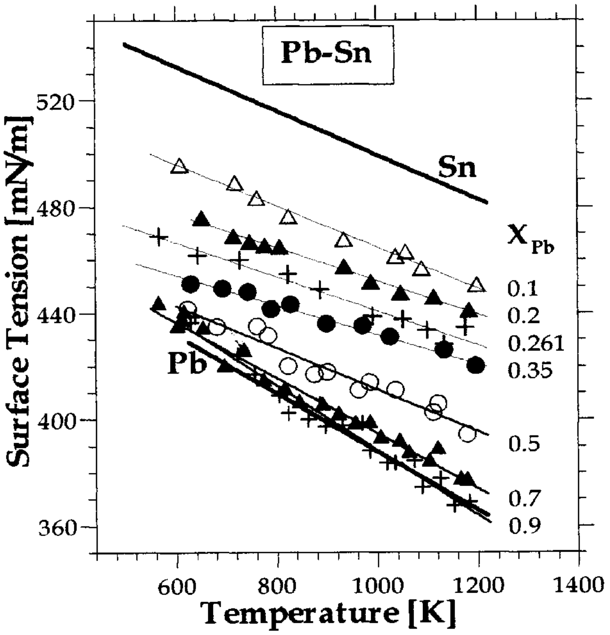

Fig. 6 Temperature dependencies of surface tension of Pb-Sn liquid alloys. Points are experimental data from this study, and straight lines are values calculated from equations shown in Table 2

represented by points with a linear dependence calculated from the equation given in Table 2 shown by a bold line. Data of this study are similar to those of [1977Kuc], [1934Bir], [1971Whi], [1989Nog], and [1971Lan] with differences not greater than 5% and with similar temperature coefficients, except for the data of [1971Lan]. The maximum deviation (about 40 mN/m, ~7%) is between the data of [1990Pas] and this study and occurs near the melting temperature of tin. This difference decreases at higher temperatures and is negligible near 1200 K. The results of [1957Hoa] exhibit nearly the same slope as the present data, being consistently higher by about 30 mN/m.

The surface tension of Pb from the present work is shown in Fig. 5 with experimental data shown as points and with the linear fits from Table 2 shown as bold lines. Literature data, [1957Hoa], [1971Lan], [1934Bir], [1959Pok], [1975Abd], [1971Whi], and [1972Ada], are included. Near 600 K, agreement between the surface tensions of the present study is within 2.5% of those from [1934Bir], [1959Pok], and [1971Whi], but with a temperature increase, the differences become higher to about 7.5% at 1000 K. At 1000 K, the data of [1957Hoa] and [1972Ada] are almost identical with those measured in this work, but at that temperature, the values of [1975Abd] are lower than the present values by about 10 mN/m or 2.5%. Differences greater than 10% are observed when comparing the present data with data of [1957Hoa] at temperatures close to 600 K. The results of [1971Lan] extrapolated to higher temperatures (1200 K) reach values very similar to those measured in this work.

The temperature dependencies of the surface tension measurements of both pure components and Pb-Sn liquid alloys are shown in Fig. 6 together with values calculated from the linear equations gathered in Table 2. The combined dependence of Pb-Sn liquid alloys on temperature and composition was filled to the following relation:

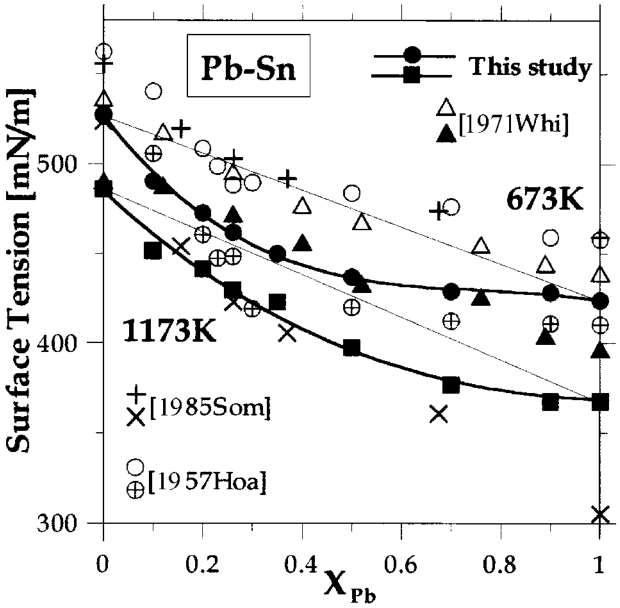

Fig. 7 Surface tension isotherms of Pb-Sn liquid alloys calculated at 673 and 1173 K in comparison with the data from the literature

$$\sigma = \sigma_{Pb}X_{Pb} + \sigma_{Sn}X_{Sn} + (-406.6 + 0.2257T)X_{Pb} + (826.8 - 0.5526T)X_{Pb}^2 + (-420.4 + 0.3270T)X_{Pb}^3 \text{ (mN/m)} \qquad \text{(Eq 4)}$$

with values of the surface tension at 673 and 1173 K from the linear equations in Table 2. The standard deviation amounts to approximately 6 mN/m (~1 to 2%).

The isotherms of the surface tension of Pb-Sn liquid alloys calculated from Eq 4 (curves) and from experiment (points) are presented in Fig. 7.

3.1 Modeling of the Surface Tension

The thermodynamic models for prediction of the surface tension have been recently discussed by Tanaka *et al.* [1994Tan, 1996Tan, 1999Tan]. The best agreement between the calculated and the experimental values was observed with Butler's equation [1932But] derived by assumption of a thermodynamic equilibrium between a bulk phase and a monolayer regarded as an individual phase. The equation, in the case of Pb-Sn, has the following form:

$$\sigma = \sigma_{Pb} + \frac{RT}{A_{Pb}} \ln \frac{(1 - X_{Sn}^S)}{(1 - X_{Sn}^B)} + \frac{1}{A_{Pb}} [G_{Pb}^{E,S}(T,X_{Sn}^S) - G_{Pb}^{E,B}(T,X_{Sn}^B)] (mN/m) \qquad \text{(Eq 5)}$$

$$= \sigma_{Sn} + \frac{RT}{A_{Sn}} \ln \frac{X_{Sn}^S}{X_{Sn}^B} + \frac{1}{A_{Sn}} [G_{Sn}^{E,S}(T,X_{Sn}^S) - G_{Sn}^{E,B}(T,X_{Sn}^B)] \ (mN/m)$$

where R is the gas constant in J/mol K; T is the temperature in Kelvin; σ_{Pb} and σ_{Sn} are, respectively, the surface tensions of pure lead and tin in mN/m; A_i is the partial molar surface area in a monolayer of components (i = Pb, Sn) in m^2; and X_{Sn}^{S} and X_{Sn}^{B} are the mole fractions of Sn in the surface and the bulk phase, respectively.

Approximating the partial molar surface as the molar surface area A_i, the monolayer is calculated from the relation

$$A_i = LN^{1/3}V_i^{2/3} \ (\mathrm{m^2/mol}) \qquad \text{(Eq 6)}$$

where N is the Avogadro's number; V_i is the molar volume of component i in m^3 calculated from the densities of pure components (Table 1); L is usually set to be 1.091 for liquid metals assuming close-packed structures; and $G_i^{E,S}$ (T, X_i) and $G_i^{E,B}$ (T, X_i) are the partial excess Gibbs energies of component i in the surface and bulk phase as a function of T and X_i, respectively.

The relationship between excess Gibbs energy in the bulk and surface phases is assumed to have the following form:

$$G_i^{E,S}\,(T,X_i^S) = \beta G_i^{E,B}\,(T,X_i^B) \ (\mathrm{J/mol}) \qquad \text{(Eq 7)}$$

where β is a parameter corresponding to the ratio of the coordination number in the surface phase to that in the bulk phase Z^S/Z^B, and it is assumed that $\beta = 0.83$ for liquid metals [1996Tan].

Calculations of the surface tension for liquid Pb-Sn alloys by means of the Butler's method (Eq 5) were performed using the values of partial excess Gibbs energies of Pb and Sn from the optimized thermodynamic parameters [1988Kar], while the data of molar volume were obtained from the densities of Sn and Pb measured by [1977Kuc] and cited in [1983Smi], respectively. The obtained results are shown in Fig. 8 and 9. Figure 8 presents a comparison of the surface tensions calculated by Butler's method (solid lines) with the experimental data, and Fig. 9 shows the isotherms of the surface tensions. In each case, the agreement between calculations and experimental data is acceptable and the differences are lower than 4%.

4. Conclusions

It has been found that the temperature dependence of the surface tension and the density of the Pb-Sn liquid alloys are linear in the temperature range from 573 to 1200 K.

The calculated isotherms of the surface tension at 673 and 1173 K exhibit negative deviations from linearity, which decrease with the temperature increase and are lower than 9% at 673 K and 7% at 1173 K.

Contrary to the surface tension, the density isotherms show positive deviations from linearity except for the alloys of the compositions from pure Sn to 0.26 mol fraction of Pb at 1173 K, where a practically linear behavior is observed.

The molar volume isotherms of Pb-Sn liquid alloys show positive deviations from the ideal behavior over the entire range of concentration and at lower 673 K, and at 1173 K and for X_{Pb} = 0 to 0.4, but at 1173 K, the deviation becomes positive above X_{Pb} = 0.4.

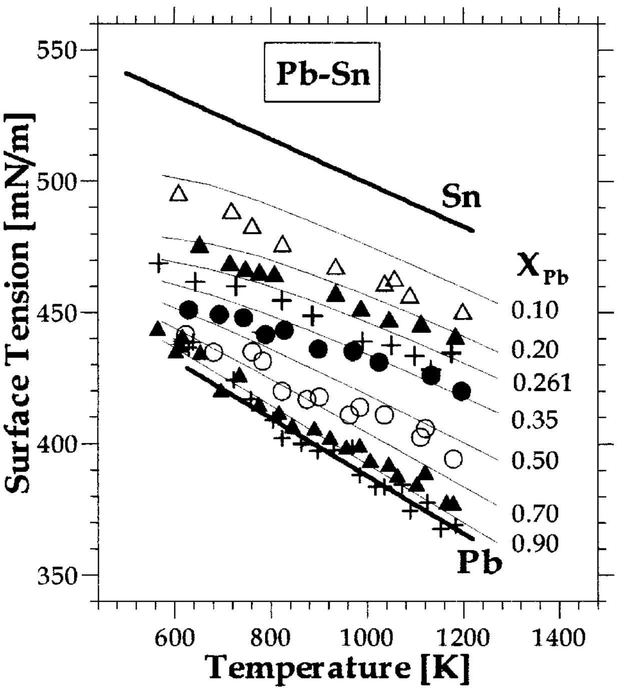

Fig. 8 Temperature dependencies of the surface tension of Pb-Sn liquid alloys calculated from Butler's relation (Eq 5) and those obtained in this study

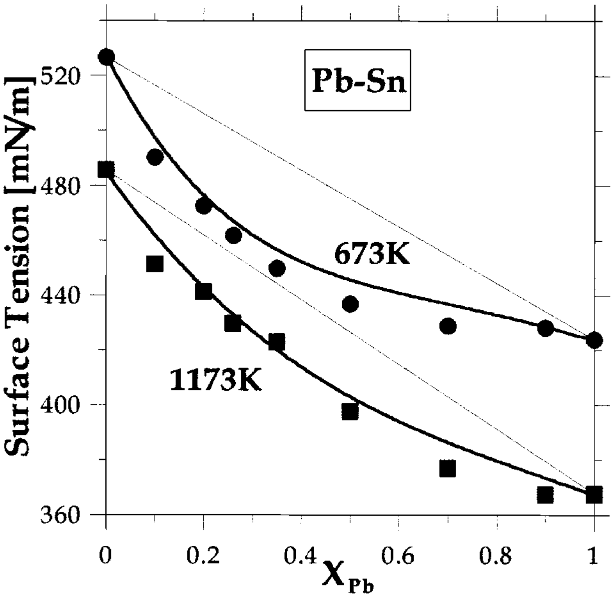

Fig. 9 Comparison of the surface tension isotherms calculated from Butler's relation (Eq 5) and those obtained in this study. Points are the experimental data from this work, and lines present values calculated from Eq 5

The minimum of the surface tension for the eutectic composition obtained by [1985Som] has not been confirmed in this study nor in those of Hard and Melford [1957Hoa] and White [1971Whi].

The surface tension between 523 and 1200 K calculated from the Butler's model shows good agreement with the experimental data and the maximum differences are lower than 4%. However, calculated temperature dependencies of the surface tension are curvilinear, which is not confirmed by experimental data.

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