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SURFACE TENSION AND DENSITY MEASUREMENTS OF LIQUID Sn-Zn ALLOYS. EXPERIMENT VS. SURDAT DATABASE OF Pb-FREE SOLDERS

POMIARY NAPIĘCIA POWIERZCHNIOWEGO I GĘSTOŚCI CIEKŁYCH STOPÓW Sn-Zn. EKSPERYMENT VS. BAZA DANYCH SURDAT LUTOWI BEZOŁOWIOWYCH

Surface tension and density of pure liquid Zn and liquid Sn-Zn alloys were measured by the maximum bubble pressure method and dilatometric technique. Measurements were undertaken at the wide range of temperature and concentrations and introduced into SURDAT database. Electronic version of the SURDAT database enables graphical presentations of the temperature dependencies of surface tension and density, isotherms of both properties and isotherm of molar volume. Experimental data of surface tension were compared with the calculations using B u t l e r ' s method.

Pomiary napięcia powierzchniowego i gęstości ciekłego cynku i ciekłych stopów Sn-Zn zostały przeprowadzone metodą maksymalnego ciśnienia w pęcherzykach gazu i techniką dylatometryczną. Pomiary wykonano w szerokim zakresie temperatur i stężeń badanych stopów wprowadzono do bazy SURDAT. Elektroniczna wersja tej bazy umożliwia graficzną prezentację temperaturowej zależności napięcia powierzchniowego i gęstości oraz w formie izoterm, jak również izotermy objętości molowej. Doświadczalne wartości napięcia powierzchniowego zostały porównane z obliczeniami modelem B u t l e r ' a.

1. Introduction

The development of Pb-free solders has been an important issue for a decade in the electronic packaging industry. It was due to the fact that the European Union RoHS (Restriction of Hazardous Substances in Electrical and Electronic Equipment) Directive will substitute lead (Pb) from all new electronic products distributed in Europe starting in July 2006 [1]. At the Institute of Metallurgy and Materials Science of the Polish Academy of Sciences extensive research and development works were initiated in 1998 and concentrated on wettability and phase equilibria studies of new alloys intended as substitute materials for traditional Sn-Pb solders, and on diffusion soldering. In the wettability studies and calculations of new phase equilibria the results of experimental thermodynamics were used to determine the thermodynamic parameters for modeling of the surface tension and for calculation of phase diagrams. Diffusion soldering is a new complementary technique in Pb-free soldering technology using the sequence of formation of intermetallic compounds in new solder joints and it often covers the gap between the low-melting and the hard solders. These extensive studies are realized within COST 531 Action, ELFNET international network, cooperation with the industrial institutes and the Tohoku University in Japan. Wettability studies of surface tension, density and modeling of surface tension enabled the creation of SURDAT database of pure components, binary and multicomponent alloys with such constituents as Sn, Bi, Sb, Cu, Zn, and In which form low melting eutectics similar to traditional Sn-Pb solders [2].

In recent years, wettability studies were carried out on two eutectics accepted as the main substitute for Sn-Pb soldering materials: Sn-Ag (m.p.221°C) and Sn-Ag-Cu (m.p.217-219°C) have the melting point higher than that of Sn-Pb (m.p.183°C), and therefore, require for industrial application higher soldering temperature. In addition, Sn-Pb has a lower surface tension than both the mentioned eutectics, indicating the need to search for materials with the properties closer to the traditional solders. Initiated at the Institute of Metallurgy and Materials Science of the Polish Academy of Sciences in Kraków, systematic measurements of the surface tension and density of Pb-free soldering materials by the maximum bubble pressure and dilatometric methods are intended for

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practical application [3] and were combined with modeling by the Butler method [4], based on optimized thermodynamic parameters supported by ADAMIS thermodynamic database developed at the Tohoku University, Sendai, Japan [5].

In recent years, the cooperation with the Tohoku University has been extended by including multicomponent alloys basing on ternary solders close to $(Sn\text{-}Ag\text{-}Cu)_{eut}$ with Sb [20] and separately on $(Sn\text{-}Ag\text{-}Cu)_{eut}$+ Bi [32] and finally on $(Sn\text{-}Ag\text{-}Cu)_{eut}$ with Bi + Sb [11], including phase diagram calculations and simulation of solidification. An example are the studies of Bi additions starting from binary eutectic Sn-Ag and ending on quaternary alloys [21, 24, 38]. It was documented that modification of the ternary Sn-Ag-Cu eutectic alloy or alloys close to this composition Sn2.76Ag0.46Cu and Sn3.13Ag0.74Cu (in at.%) are very sensitive to the Bi additions, and should not exceed 1–3.5 mass% of Bi. This is also in agreement with Hwang [30] analysis, still retaining within the wettability studies the distance to properties of traditional solders Sn-Pb.

The current studies on Pb-free solders are concentrated on the metric of wettability employing in addition to Sn-Ag-Cu-Bi [21, 24] also the quinary alloys Sn-Ag-Cu-Bi-Sb [11] combining surface tension in protective atmosphere with interfacial tension and surface tension measured in air including the meniscographic technique providing the wetting time, wetting force and contact angles. These studies confirmed the conclusions of Lopez et al. [25] indicating for the metric of wettability the importance of interfacial tension with contact angles measured in air and surface tension with contact angles measured in protective atmosphere.

Nearly two years ago, in parallel to wettability studies on both eutectics Sn-Ag and Sn-Ag-Cu there were initiated measurements of new Pb-free solders starting from eutectic Sn-Zn. The melting point of Sn14.9Zn atomic % is close to that of the Sn-Pb eutectic solder. Moreover, Sn-14.9 Zn atomic % solder has excellent ductility, which makes processing easy [26]. On the other hand, the wettability of Sn14.9Zn atomic % solder is higher than that of Sn-Pb eutectic and in addition Zn is more rapidly oxidized than Pb [27].

In order to improve the wettability and to lower the melting point, In is added to Sn-Zn solder as reported by McCormack and Jin [28]. Due to these indications, within PhD thesis [33] there were undertaken wettability studies on Sn-Zn-In ternary liquid alloys aimed at:

1. Experimental determination of surface tension, density and contact angles including also modeling by the Butler method [4] of Sn-Zn-In alloys together with the constituent binaries, Sn-Zn, Zn-In and In-Sn,
2. These new data, both experimental and from modeling will be included into the SURDAT database,
3. On the example of Sn-Zn it will be documented how the starting experimental data are introduced into SURDAT [29] and how they are processed to produce the standard plots of physical properties and equation describing temperature and concentration dependence of the surface tension using Butler method.

Preliminary measurement results of the physical properties of Zn-Sn and Zn-In binary liquid alloys were presented during the TOFA conference in 2004, and of In-Sn during the mid- term workshop of COST 531 in Genoa 2006 [34]. Thermodynamic and physical properties of liquid In-Sn alloys are particularly interesting as on the one hand, surface tension and density data of pure components In and Sn are very similar, due to this we are not observing the change when In is added to Sn or vice versa [14], but on the other hand, the isotherms of surface tension [34], viscosity [35] and resistivity [36] reflect the "S" shape characteristic of structural changes.

There is another indication of the mutual correlations of thermodynamic properties, with physical properties and the structural changes of liquid alloys – the area in which two departments located at the Institute of Metallurgy and Materials Science of the Polish Academy of Sciences have been working since the Krupkowski's binary formalism was presented in the early 50^{th} of the last century [37].

Within a PhD thesis similar measurements of surface tension and density are continued for ternary alloys Sn-In-Zn at four cuts in Gibbs composition triangle with constant ratio X_{Sn}/X_{In}.

2. Surface tension and density of liquid Sn-Zn alloys

During TOFA Conference [16] the results of surface tension and density measurements performed at extensive range of temperature were presented in the form of two tables, Table 1 and Table 2. The experimental results were fitted by the least square method, and the first two columns of these tables comprising concentrations of investigated alloys and the linear equations are usually introduced into SURDAT database. It is also possible to use a separate program for averaging of the original experimental points.

TABLE 1

Temperature dependencies of the surface tension of liquid Sn-Zn alloys with calculated errors of the A and B parameters and the surface tension calculated at 773 K

X_{Zn}	$\sigma = A + BT$ $mN \cdot m^{-1}$	$\sigma_{(773K)}$ $mN \cdot m^{-1}$	Err(A) $mN \cdot m^{-1}$	Err(B) $mN \cdot m^{-1} \cdot K^{-1}$
1.0000	892.5–0.1246T	796.2 ± 11.4	± 34.7	± 0.0421
0.9000	767.8–0.0952T	694.3 ± 5.9	± 20.3	± 0.0232
0.7000	694.8–0.0936T	622.4 ± 4.0	± 10.1	± 0.0121
0.5000	682.4–0.1321T	580.2 ± 9.3	± 21.4	± 0.0241
0.3000	624.2–0.1010T	546.1 ± 9.9	± 17.0	± 0.0196
0.1000	599.8–0.0791T	538.6 ± 7.6	± 10.8	± 0.0128
0.0000*	582.8–0.0834T	518.4 ± 9.2	± 6.6	± 0.0079

* based on Ref. [7]

TABLE 2

Temperature dependencies of the density of liquid Sn-Zn alloys with calculated errors of the A and B parameters and the density calculated at 773 K

X_{Zn}	$\rho = A + B^*T$ $g \cdot cm^{-3}$	$\rho_{(773K)}$ $g \cdot cm^{-3}$	Err(A) $g \cdot cm^{-3}$	Err(B) $g \cdot cm^{-3} \cdot K^{-1}$
1.0000	7.1015–0.000820T	6.468 ± 0.040	± 0.116	± 0.000130
0.9000	7.1048–0.000775T	6.506 ± 0.046	± 0.161	± 0.000187
0.7000	7.1558–0.000776T	6.556 ± 0.031	± 0.109	± 0.000128
0.5000	7.1511–0.000651T	6.648 ± 0.018	± 0.056	± 0.000068
0.3000	7.2363–0.000663T	6.724 ± 0.029	± 0.067	± 0.000082
0.1000	7.2697–0.000630T	6.782 ± 0.032	± 0.071	± 0.000089
0.0000*	7.3120–0.000615T	6.836	–	–

* based on Ref. [38]

3. Presentation of surface tension and density data employing SURDAT database

There is a usual presentation of experimental data for all pure components and alloys intended as the substitute for Sn-Pb solders in the form of seven main plots presented below for liquid Sn-Zn alloys.

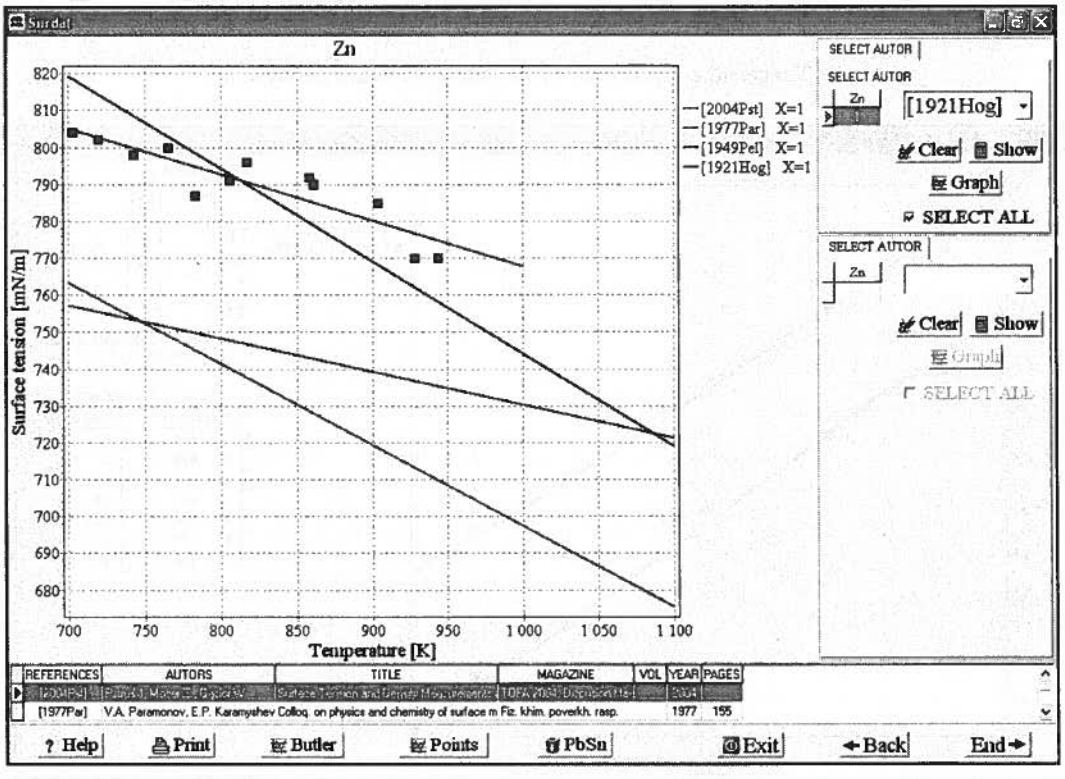

Fig. 1. Temperature dependence of the surface tension of liquid Zn compared with various references

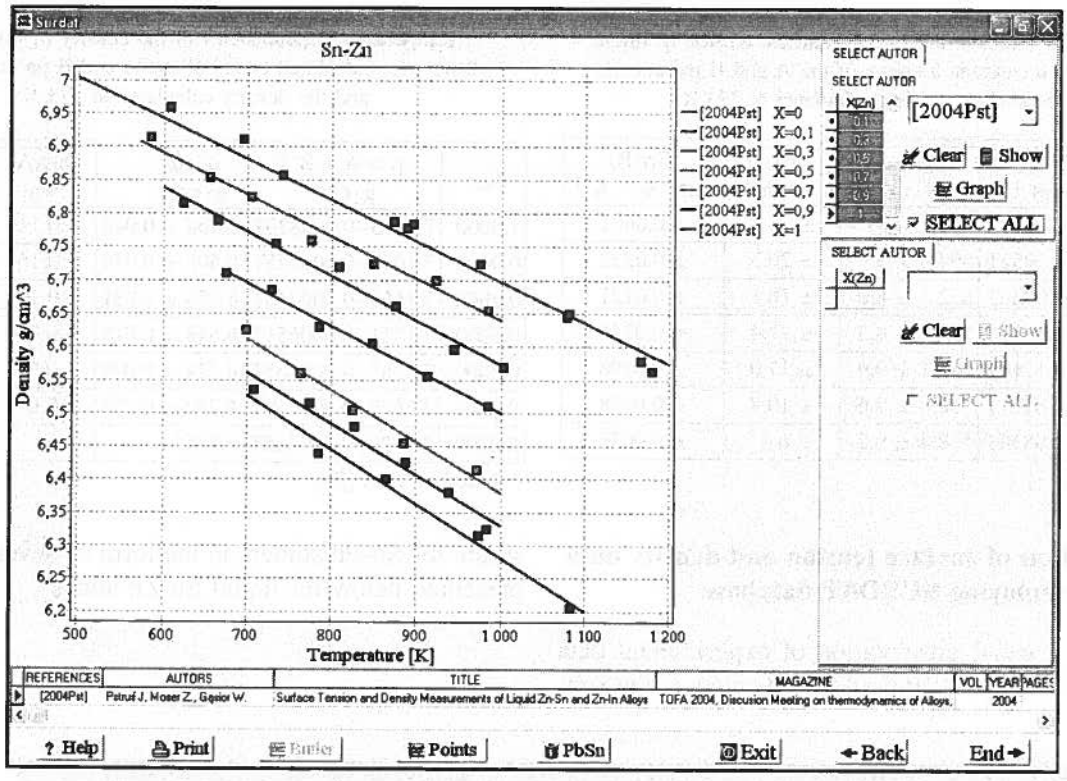

Fig. 2. Temperature dependence of the density of liquid Sn-Zn alloys

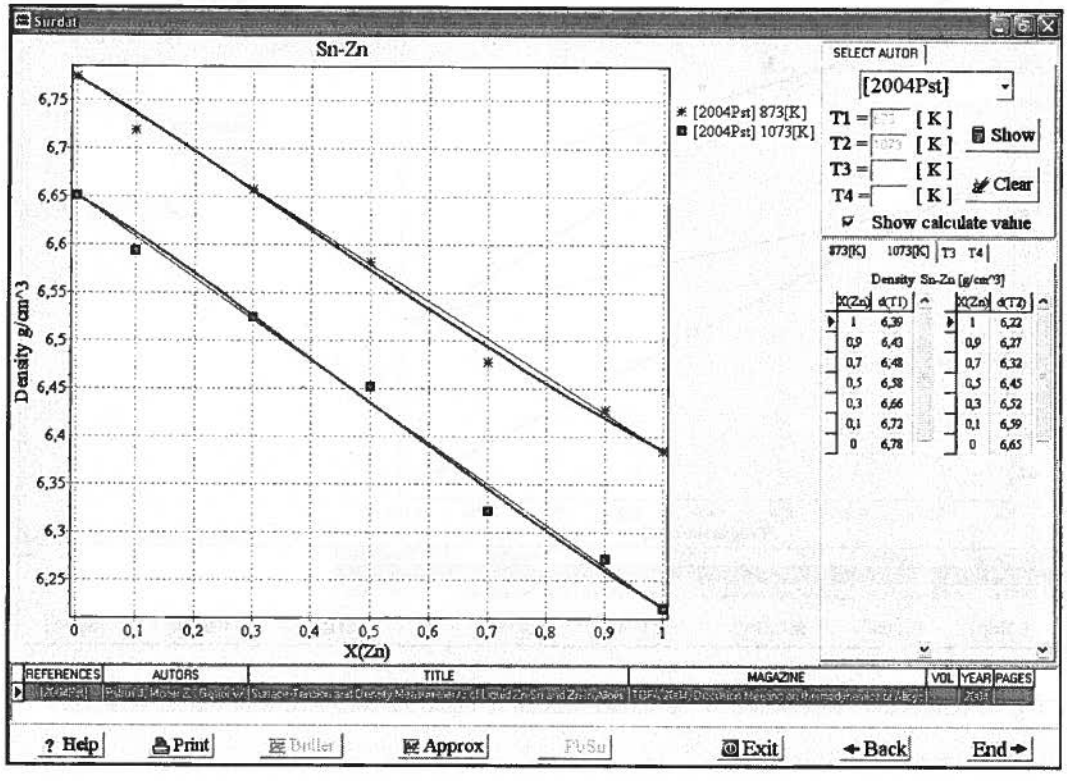

Fig. 3. Isotherms of the density of liquid Sn-Zn alloys

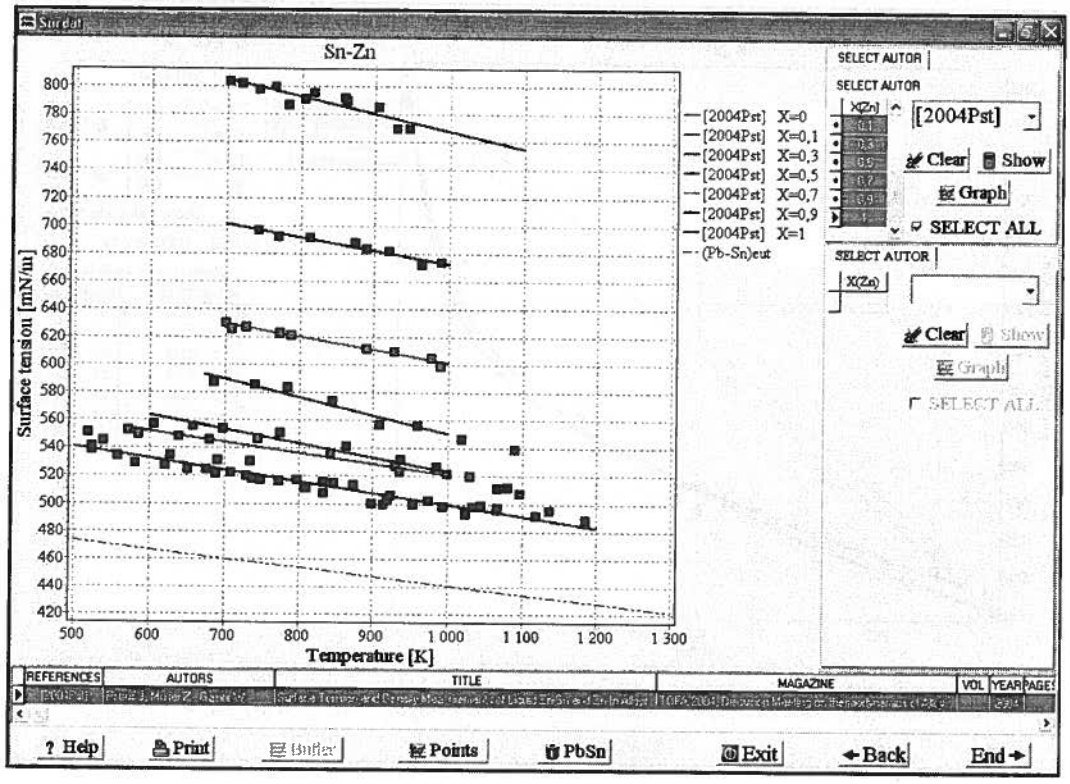

Fig. 4. Temperature dependencies of the surface tension of liquid Sn-Zn alloys

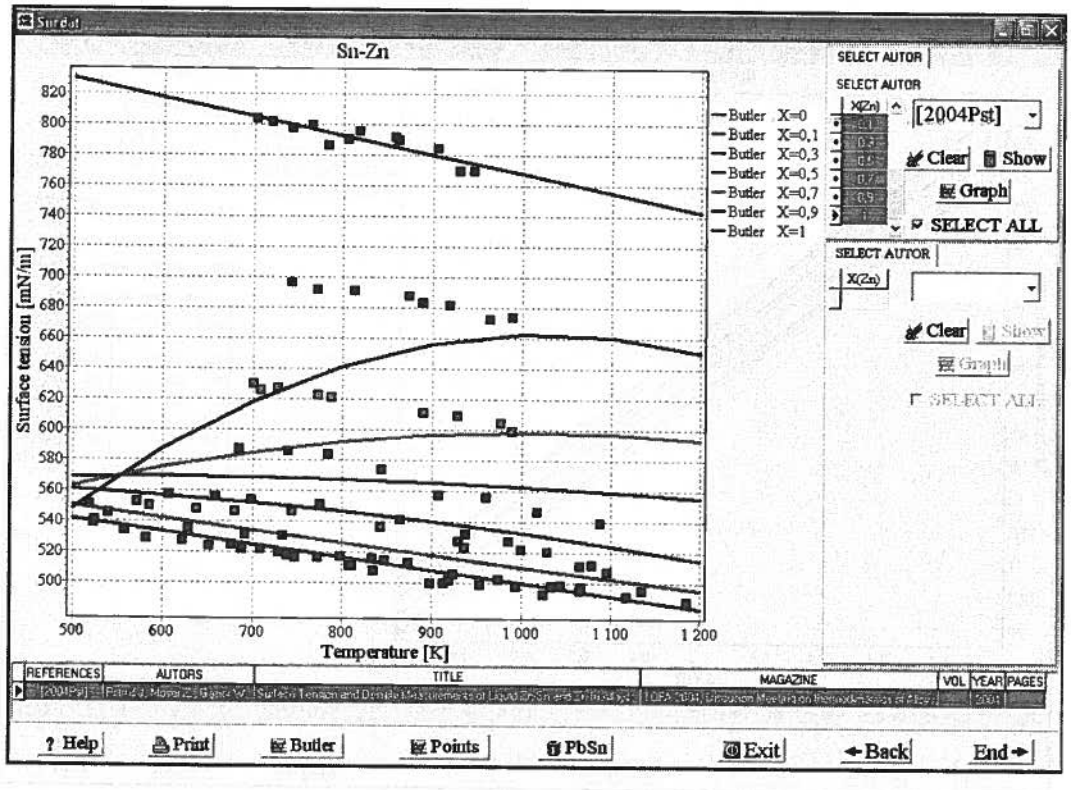

Fig. 5. Temperature dependencies of the surface tension of liquid Sn-Zn alloys (experimental points) compared with Butler's modeling (solid lines)

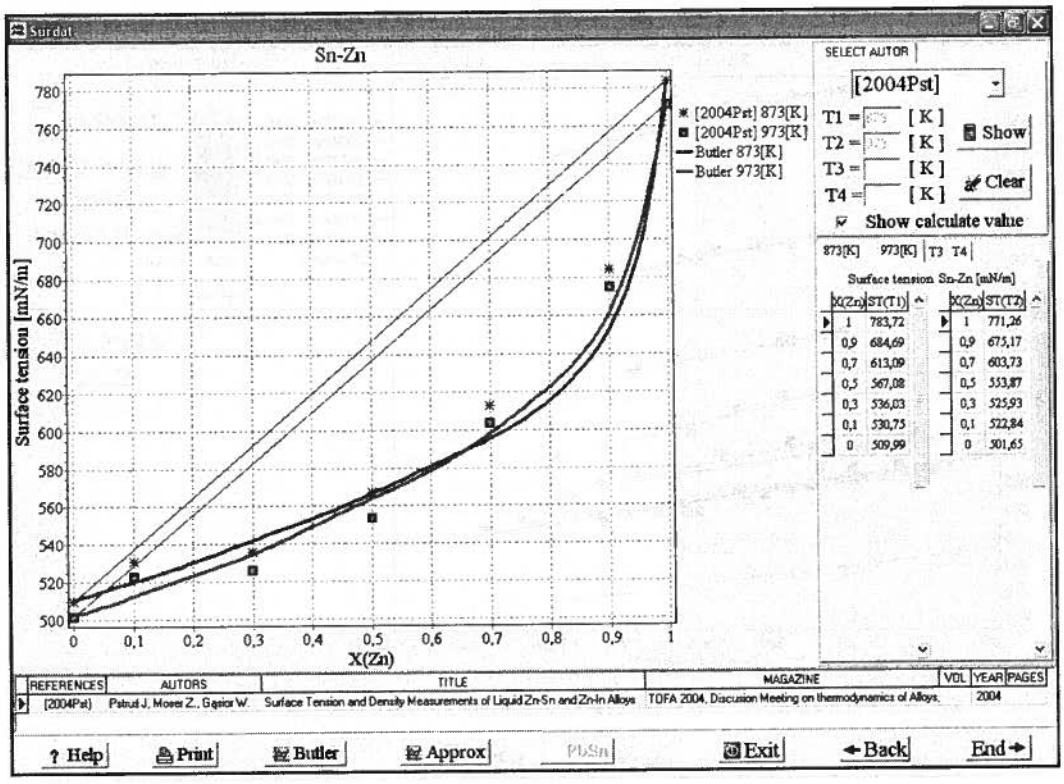

Fig. 6. Isotherms of the surface tension of liquid Sn-Zn alloys (experimental points) compared with Butler's modeling (solid lines) at 873 K and 973 K

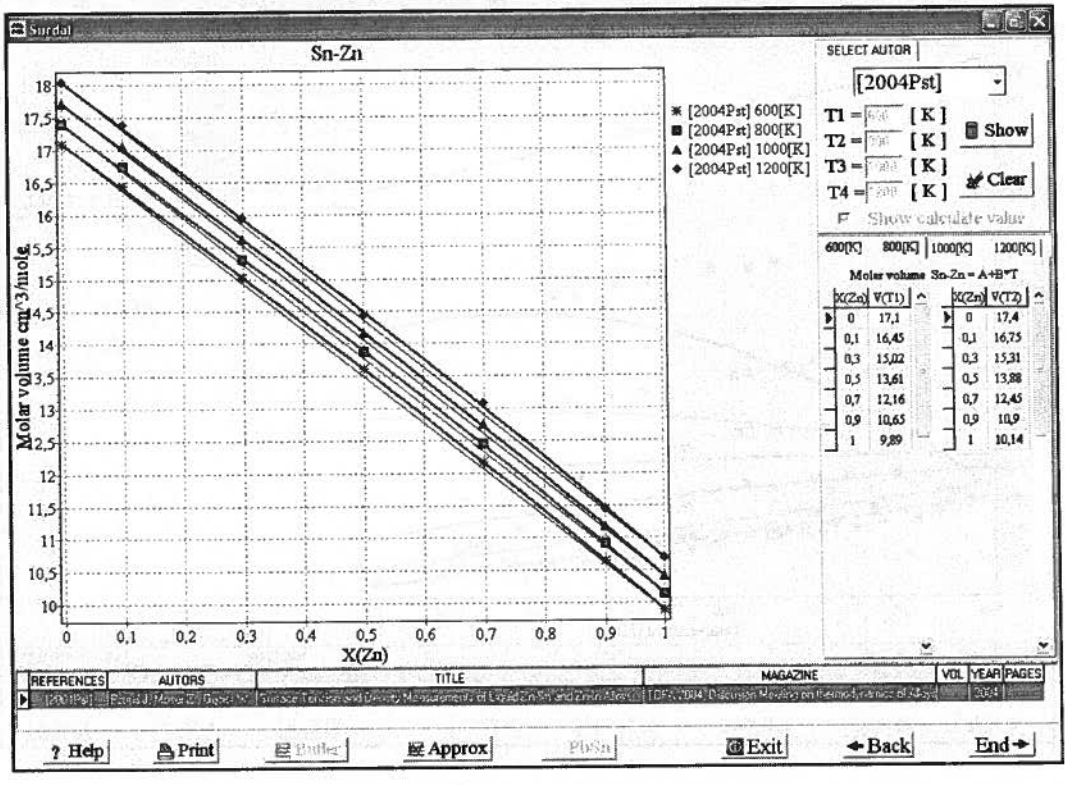

Fig. 7. Isotherms of the molar volumes of liquid Sn-Zn alloys calculated at 600 K, 800 K, 1000K and 1200 K

Electronic version of SURDAT database [29] enables the same presentation for all previously investigated alloys and pure components listed in Table 3.

TABLE 3
Summary of the investigated systems of Pb – free alloys

Metals	Ref.	Binary alloys	Ref.	Multicomponent alloys	Ref.
Pb	[6]	Pb-Sn	[6]	$(Sn-Ag)_{eut}$ + Zn	*
Sn	[7]	Ag-Sn	[7]	$(Sn-Ag)_{eut}$ + In	[14]
In	[8]	Ag-In	[8]	$(Sn-Ag)_{eut}$ + Bi	[9]
Ag		Bi-Sn	[9]	$(Sn-Ag)_{eut}$ + Cu	[18]
Bi	[9]	In-Sn	[14]	$(Sn-Ag)_{eut}$ + Sb	[19]
Sb	[10]	Ag-Bi	[15]	$(Sn-Ag)_{eut}$ + Cu + Sb	[20]
Cu	[11]	Sb-Sn	[10]		[23]
Zn	[16]	In-Zn	[16]	$(Sn-Ag)_{eut}$ + Cu + Bi	[17]
Al.	[12]	Sn-Zn			[21]
Au	[13]	Ag-Sb	[17]		[24]
		Cu-Sn		$(Sn-Ag-Cu)_{eut}$ + Bi + Sb	[11]
		Cu-Sb			[21]

* not published

In addition, a separate program compiled for Butler's modeling employs the excess G i b b s energies of liquid components of the investigated solders and data of surface tension of pure metals to calculate the surface tension and next to elaborate the results in the form of an equation of the temperature and concentration dependence. In the case of liquid Sn-Zn alloys such a relation has the following form:

$$\sigma = 892.5 - 0.124632T * X_{Zn} /(X_{Zn} + X_{Sn}* 8.57751942 - 0.00702796085*T + 0.00141219317*T*\ln(T) - 7.47606782E-006*T^2 - 28.7789993 + 0.0277582332 *T-0.00442097662*T*\ln(T) + 2.61775749E - 005* T^2)*X_{Zn} + (117.320076 - 0.14574009*T - 0.00304485275*t*\ln(T) + 5.74244696E - 005*T^2)* X_{Zn}^2) + 582.8 - 0.0833615T *(X_{Sn}/(X_{Zn} + X_{Sn} * 8.57751942 - 0.00702796085*T + 0.00141219317*T*\ln(T) - 7.47606782E - 006*T^2 - 28.7789993 + 0.0277582332 *T - 0.00442097662*T*\ln(T) + 2.61775749E - 005* T^2)*X_{Zn} + (117.320076 - 0.14574009*T - 0.00304485275*T*\ln(T) + 5.74244696E - 005*T^2)* X_{Zn}^2))$$

Standard Deviation = 2.1 mN/m

From this relation, the data of the surface tension of liquid Sn-Zn alloys in Fig. 5 are compared with experimental results. The calculated results from the Butler model show some deviations in comparison with experimental points, particularly at higher concentrations of Zn, which may result from difficulties in obtaining experimental thermodynamic functions of liquid Sn-Zn alloys, requiring a new model of the mono-atomic surface area and a new relation between surface and the bulk excess free energy. Experimental data of surface tension of Zn [43] and [44] and surface tension of liquid Sn-Zn alloys [44] were not taken into consideration as showing the curvilinear temperature dependence.

4. Conclusions

SURDAT database is prepared to supply surface tension, density, molar volumes and the modeled values of surface tension of all listed in Table 3 pure components and alloys, the possible candidates for Pb-free solders. It includes also the results of liquid Sn-Zn alloys, being one of the constituent binaries of the ternary Sn-Zn-In system investigated within a doctor's thesis by Pstruś [33].

To model the surface tension, Butler's method was used with thermodynamic parameters of liquid Sn and Zn from ADAMIS database [5]. B u t l e r ' s thermodynamic modeling is a useful approximation to the surface tension measured in protective atmosphere, and offers preliminary indication of the influence of a given addition on decrease or increase of the wettability. It should be noted however, that the calculated temperature dependence of the surface tension is slightly curvilinear in comparison with the straight linear dependence of experimental data. This problem was discussed in the case of Ag-Bi [15] liquid alloys suggesting the temperature dependence of the parameters existing in B u t l e r ' s model.

In the case of the experimental data of the surface tension of liquid Sn-Zn alloys the additional problem is connected with the evaporation of Zn, particularly observed in alloys rich in Zn. Due to reasonable agreement with experimental data, in all tested candidates to substitute the traditional Sn-Pb solders we have used B u t l e r ' s method to create the SURDAT database of surface tension, density and modeling of the surface tension.

This report opens the gate for the new Pb-free solders based on Sn-Zn eutectic and after completing the studies of Sn-Zn-In alloys research will be continued on Ag addition [31] improving the mechanical properties.

SURDAT database in preparation for print as a monograph, edited by the Institute of Metallurgy and Materials Science [29], will present in electronic form, for all listed systems in Table 3, the physical properties of candidates for Pb-free materials, being an example of Polish contribution to the research of replacement of traditional Sn-Pb solders.

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Note: References in the SURDAT database are presented as: Year, first three letters of the first author's name. Therefore, in some listed References there appear number, and in addition Reference as accepted in the SURDAT database.

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