Thermal and concentration dependence of surface tension and melt density of indium-tin-lead-bismuth system

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Abstract. The study of behavioral patterns and changes in the surface properties of melts as the number of components increases is of great interest. The aim of the work is to reveal theoretically predicted regularities that establish the relationship between the type of isotherms of surface tension and the density of the four-component system of indium tin-lead-bismuth from the type of corresponding side double systems. In particular, indium tin systems.

1. Introduction
This paper presents the results of the experimental study of surface tension and density of the four-component indium-tin-lead-bismuth system [1, 2]. It should be noted that the surface properties of pure fusible metals and their double alloys have been studied quite fully [3–6]. There are also experimental data on many three-component systems consisting of these metals [7–9]. Of great interest was the comparative analysis of such surface properties of fusible alloys as temperature and concentration dependence of surface tension and density. An interesting result of such work was the conclusion of the authors [10] as a result of the study of the surface properties of systems made of fusible metals, namely, the features of the concentration dependence of surface tension revealed in some double systems, in particular, in the systems of indium tin, thallium lead are manifested in three-component systems where as components are present systems In-Sn, Tl-Pb, but these features disappear with the addition of a third component to these systems. This effect is observed in the triple systems of indium tin-lead, thallium-lead-bismuth, where the minimums found on the isotherms of surface tension in the lateral double systems of thallium-lead and indium tin disappear with the addition of the third component of lead and bismuth, respectively [11, 12]. In addition, it was assumed that the surface properties of the triple systems are predicted on the basis of similar properties of the lateral double melts [1, 10, 12]. In this connection, there was an interest in studying the surface properties of melts consisting of more components. The results of the study could either confirm the revealed tendency of interrelation of surface properties of double and multi-component systems, or refute the revealed regularities.

2. Methods and materials
To investigate the melts of the indium-lead-lead-bismuth system, a combined instrument developed in our laboratory was used, in which the surface tension was measured by the method of maximum droplet pressure and an advanced hydrometer was used to measure the density of the system.
Figure 1. Combined instrument for measuring surface tension and density of multi-component melts

The device makes it possible to prepare alloys of different concentrations, to study the surface tension and density \( y \) of these alloys without opening it and, consequently, without disturbing its thermal and vacuum conditions, which has a significant impact on the reliability of the experiment and productivity, as the experimenter is free from time-consuming procedures of washing, drying and long-term thermal and vacuum treatment of the device before measuring the properties of each alloy separately.

At the same time, the consumption of expensive metals is reduced by 10 times and the time of experiments is reduced to the same extent.

The following expression is used to determine the density of the hydrometer:

\[
\rho = \frac{P_0}{q(V_0 + \pi h) - \pi k R h}, \quad (1)
\]

\( P_0 \) – hydrometer weight in vacuum, \( V_0 \) – total hydrometer volume, \( R \) – capillary radius, \( r \) – rod radius, \( h \) – Distance from the liquid level to the upper end of the hydrometer rod, \( \Delta h \) – difference in fluid levels in the hydrometric cylinder and capillary outlet.

The expression (1) is true on the assumption that the capillary outlet and the hydrometer rod are strictly cylindrical, but in practice the rods and capillaries do not always have a cylindrical form and therefore the average values of radii are used in the calculations.

The error in the calculation of the surface tension also depends on the capillary radius, which is derived from:

\[
\frac{S_\sigma}{\sigma} = \sqrt{(\delta \rho)^2 + \left(\frac{S_\rho}{\rho}\right)^2 + \left(\frac{S_r}{r}\right)^2 + \left(\frac{S_h}{h}\right)^2}. \quad (2)
\]
The maximum error of PE measurement by the method of maximum drop pressure is 0.8%, density – 0.2%, and composition – 0.22%.

High purity metals were used for the experiment. In-00; Sn-000; Pb-0000; Bi-0000. Temperature interval of researches from temperature liquidus to 773 K.

3. Results

The side double systems that make up this four-component system are characterized by smooth surface tension isotherms, except for the indium tin system. The dependence of the surface tension on the composition in the two-component 6 indium tin system is characterized by an isotherm with a minimum peculiarity in the region of medium compositions. On the isotherms describing concentration dependences of PHs of triple melts In-Sn-Pb [12] and In-Sn-Bi [13] the peculiarity in the form of minimum is equalized by adding the third component (bismuth or lead). Thus, the concentration dependence of PN in melts of triple systems Sn-Pb-Bi, In-Pb-Bi is transmitted by a smooth curve without extremums. Calculations have shown that the dependence of PN on the composition in the side double and triple systems, which make up the quadruple system, is described with good accuracy by the polynomial of the third degree. For this reason, we use this model to study the quadruple indium-old-lead-bismuth system.

Polynomial coefficients are calculated by means of a plan that ensures uniform concentration of experimental points on a three-dimensional symphlex in the form of a correct tetrahedron. The points of the plan, as nodes of the simplex lattice and used to determine the polynomial coefficients, are shown in Figure 2.

In order to analyze and verify the compliance of the regression equation, it is necessary to obtain the surface tension values of the four-component melts. Temperature dependences of density and PN of nine four-component melts, the compositions of which are located at the radial section originating at the top of the tetrahedron corresponding to bismuth, have been studied for this purpose. The obtained results are presented in Table 1.

![Figure 2. Scheme of the experiment for the third order model](image-url)
The values of the regression equations at temperatures of 623 K and 773 K, as well as the experimental values of PN for pure metals and alloys used to determine the regression coefficients are given in Table 2.

**Table 1.** \( \rho \) (kg/m\(^3\)) and \( \sigma \) (mДж/m\(^2\)) of In-Sn-Pb-Bi melts

| \( X_{\text{Bi}} \) | \( X_{\text{In}} \) | \( X_{\text{Sn}} \) | \( X_{\text{Pb}} \) | \( \rho \) | \( \sigma \) | \( \rho \) | \( \sigma \) |
|----------------|----------------|----------------|----------------|--------|--------|--------|--------|
| 0.00 | 0.33 | 0.33 | 0.34 | 8.877 | 426 | 8.850 | 475 |
| 0.06 | 0.31 | 0.31 | 0.32 | 8.905 | 459 | 8.888 | 458 |
| 0.14 | 0.28 | 0.28 | 0.30 | 8.937 | 451 | 8.907 | 450 |
| 0.22 | 0.25 | 0.25 | 0.28 | 8.991 | 440 | 8.952 | 439 |
| 0.29 | 0.22 | 0.22 | 0.27 | 9.017 | 432 | 8.990 | 430 |
| 0.34 | 0.21 | 0.21 | 0.24 | 9.062 | 425 | 9.020 | 423 |
| 0.40 | 0.19 | 0.19 | 0.22 | 9.075 | 420 | 9.055 | 419 |
| 0.43 | 0.18 | 0.18 | 0.21 | 9.126 | 417 | 9.126 | 417 |
| 0.50 | 0.16 | 0.16 | 0.18 | 9.288 | 416 | 9.224 | 415 |
| 0.54 | 0.15 | 0.15 | 0.15 | 9.302 | 409 | – | 409 |
| 0.57 | 0.14 | 0.14 | 0.15 | – | – | 9.433 | 407 |
| 0.63 | 0.12 | 0.12 | 0.13 | – | – | 9.494 | 400 |
| 0.72 | 0.09 | 0.09 | 0.100 | – | – | – | – |
| 0.82 | 0.056 | 0.056 | 0.064 | 8.999 | 406 | – | 400 |
| 0.86 | 0.044 | 0.044 | 0.050 | 9.075 | 403 | – | 403 |
| 0.947 | 0.017 | 0.017 | 0.198 | – | – | – | – |
| 1.00 | 0 | 0 | 0 | – | – | – | – |
| 0.00 | 0.33 | 0.33 | 0.34 | 8.816 | 474 | 8.785 | 472 |
| 0.06 | 0.31 | 0.31 | 0.32 | 8.857 | 457 | 8.829 | 455 |
| 0.14 | 0.28 | 0.28 | 0.30 | 8.884 | 448 | 8.860 | 447 |
| 0.22 | 0.25 | 0.25 | 0.28 | 8.933 | 436 | 8.903 | 435 |
| 0.29 | 0.22 | 0.22 | 0.27 | 8.951 | 428 | 8.922 | 427 |
| 0.34 | 0.21 | 0.21 | 0.24 | 8.996 | 422 | 8.965 | 420 |
| 0.40 | 0.19 | 0.19 | 0.22 | 9.020 | 418 | 8.990 | 415 |
| 0.43 | 0.18 | 0.18 | 0.21 | 9.083 | 415 | – | 412 |
| 0.50 | 0.16 | 0.16 | 0.18 | 9.146 | 411 | 9.066 | 408 |
| 0.54 | 0.15 | 0.15 | 0.16 | 9.286 | 409 | 9.177 | 404 |
| 0.57 | 0.14 | 0.14 | 0.15 | 9.343 | 402 | 9.287 | 399 |
| 0.63 | 0.12 | 0.12 | 0.13 | 9.46 | 398 | 9.400 | 395 |
| 0.72 | 0.09 | 0.09 | 0.100 | 9.560 | 393 | 9.500 | 388 |
| 0.82 | 0.056 | 0.056 | 0.064 | 9.705 | 386 | 9.663 | 384 |
| 0.86 | 0.044 | 0.044 | 0.050 | 9.776 | 383 | 9.737 | 381 |
| 0.947 | 0.017 | 0.017 | 0.198 | 9.888 | 379 | 9.811 | 376 |
| 1.00 | 0 | 0 | 0 | 9.965 | 376 | 9.952 | 375 |
| 0.00 | 0.33 | 0.33 | 0.34 | 8.722 | 469 | 8.693 | 468 |
| 0.06 | 0.31 | 0.31 | 0.32 | 8.760 | 452 | 8.715 | 449 |
| 0.14 | 0.28 | 0.28 | 0.30 | 8.798 | 423 | 8.755 | 441 |
| 0.22 | 0.25 | 0.25 | 0.28 | 8.848 | 431 | 8.815 | 429 |
| 0.29 | 0.22 | 0.22 | 0.27 | 8.860 | 423 | 8.843 | 421 |
| 0.34 | 0.21 | 0.21 | 0.24 | 8.905 | 416 | 8.875 | 414 |
| 0.40 | 0.19 | 0.19 | 0.22 | 8.920 | 412 | 8.910 | 410 |
| 0.43 | 0.18 | 0.18 | 0.21 | 8.922 | 408 | 8.926 | 407 |
| 0.50 | 0.16 | 0.16 | 0.18 | 9.003 | 404 | 8.980 | 402 |
| 0.54 | 0.15 | 0.15 | 0.16 | 9.075 | 398 | 9.044 | 396 |
| 0.57 | 0.14 | 0.14 | 0.15 | 9.205 | 394 | 9.145 | 391 |
| 0.63 | 0.12 | 0.12 | 0.13 | 9.286 | 389 | 9.246 | 387 |
| 0.72 | 0.09 | 0.09 | 0.10 | 9.408 | 383 | 9.374 | 381 |
| 0.82 | 0.056 | 0.056 | 0.064 | 9.557 | 378 | 9.513 | 376 |
| 0.86 | 0.044 | 0.044 | 0.050 | 9.620 | 376 | 9.580 | 373 |
| 0.947 | 0.017 | 0.017 | 0.198 | 9.730 | 371 | 9.688 | 368 |
| 1.00 | 0 | 0 | 0 | 9.801 | 367 | 9.758 | 365 |
Table 2. Dependence of third order polynomials on the concentration of the four-component system In-Sn-Pb-Bi

| Molar fraction composition | σ_{ijk} | β_{ijk} |
|-----------------------------|---------|---------|
| σ_{1} | 545 | 531 | 545 | 531 |
| σ_{2} | 535 | 524 | 535 | 524 |
| σ_{3} | 438 | 426 | 438 | 426 |
| σ_{4} | 374 | 365 | 374 | 365 |
| 0.66 | 0.33 | 0.33 | 0.33 | 0.33 |
| σ_{112} | 532 | 525 | β_{12} | -41 | -23 |
| σ_{122} | 530 | 520 | γ_{12} | -9 | 18 |
| σ_{113} | 476 | 470 | β_{13} | -115 | -88 |
| σ_{133} | 456 | 448 | γ_{13} | -106 | -88 |
| σ_{114} | 428 | 418 | β_{14} | -227 | -221 |
| σ_{144} | 390 | 380 | γ_{14} | -128 | -117 |
| 0.33 | 0.33 | 0.33 | 0.33 | 0.33 |
| σ_{223} | 475 | 470 | β_{23} | -104 | -83 |
| σ_{133} | 452 | 443 | γ_{23} | -63 | -38 |
| σ_{234} | 418 | 413 | β_{24} | -227 | -216 |
| σ_{244} | 390 | 380 | γ_{24} | -173 | -135 |
| 0.33 | 0.33 | 0.33 | 0.33 | 0.33 |
| σ_{334} | 410 | 395 | β_{34} | -32 | -45 |
| σ_{344} | 388 | 376 | γ_{34} | 5 | -9 |
| 0.33 | 0.33 | 0.33 | 0.33 | 0.33 |
| σ_{133} | 478 | 470 | β_{123} | 20 | -59 |
| σ_{134} | 420 | 408 | β_{134} | 247 | -828 |
| σ_{234} | 430 | 420 | β_{234} | 9 | 943 |
| 0.00 | 0.33 | 0.33 | 0.33 | 0.33 |
| σ_{234} | 416 | 404 | β_{234} | 195 | 106 |

Figure 3. PH isothermal and molar volumes in the indium-tin-lead-bismuth system

As it was expected, the isotherms of surface tension in the four-component system of indium-tin-lead-bismuth are characterized by the presence of a peculiarity in the form of a minimum connected with a similar feature (minimum) on the graphs of concentration dependence of the side two-component system of indium-tin. The existence of this feature predetermines the necessity to check the obtained equation for adequacy. In this connection, together with the data on side melts, the experimental PN isotherms for the beam section with a constant ratio of molar fractions of lead, indium and tin were used (Pb : In : Sn = 1:1:1). Comparison of experimental data on the concentration dependence of PN and calculated on the polynomials (Figure 3) showed that the experimental data and calculated values within the measurement error coincide. Also the model of the third order qualitatively describes features of influence of the fourth component on an extreme on an isothermal surface in the form of a minimum in triple systems In-Sn-Pb и In-Sn-Bi.
Thus, we managed to show that the model of the third order with sufficient accuracy reflects the real dependence of the surface tension on the composition in the studied four-component system.

Not less important is the fact that it was possible to show that the experimental values of surface tension coincide well with the PN values calculated by different theoretical equations in the assumption of the ideal solutions. The more components in the system, the better this coincidence is manifested.

Dependence of surface tension and density on temperature in the studied quadruple melt is linear with negative temperature coefficient (Figure 4, 5).

A certain interest is the concentration dependence of the temperature coefficient of surface tension on the beam section. This dependence is presented in Figure 5, from where it is seen that the isotherm $\frac{\partial \sigma}{\partial T}$ within the experimental error isotherm is described by the linear line.

**Figure 4.** Temperature dependence of In-Sn-Pb-Bi melts PH at bismuth concentrations (1-0.0; 2-0.06; 3-0.14; 4-0.22; 5-0.29; 6-0.34; 7-0.54; 8-0.82; 9-1.0) mol. fractions.

**Figure 5.** Temperature dependence of In-Sn-Pb-Bi melts density at bismuth concentrations (1-1.0; 2-0.63; 3-0.57; 4-0.4; 5-0.29; 6-0.06; 7-0.0) mol. fractions.
It should be noted that in contrast to the surface tension, the error of determining the temperature coefficient \( \sigma \) is high (up to 20 %). In our opinion, this is due to the fact that in our experiments we failed to identify the regularities of the coefficient change \( \frac{\partial \sigma}{\partial T} \) with the concentration of bismuth.

A common feature of the surface tension isotherms of the In-Sn-Pi and In-Sn-Bi triple side systems is the presence of a minimum in the area adjacent to the In-Sn concentration triangle. The study of the influence of the fourth component (bismuth or lead) on the behavior of this feature on the isothermal surface tension is particularly interesting.

For illustration of the "picture" of the dependence of physical and chemical properties on the composition of the multicomponent melt, the isolines of properties on different planes are used in order to illustrate the "picture" of the dependence of the physico-chemical property on the composition of the multicomponent melt, we use isolines of properties on different planes.

Figure 6. Concentration dependence of PN temperature coefficient in indium-tin-lead-bismuth system

Thus, Figure 7 shows the isolines of the PN sections corresponding to the planes with a constant concentration of bismuth. The diagrams clearly show how the bismuth content affects the type of isothermal surface tension of the triple indium-tin-lead system. It can also be seen from the graphs that at a low bismuth content (less than 0.05 mol. fractions) the minimum on the isothermal surface is equalized. Further increase of bismuth content does not result in qualitative change of the isothermal surface shape.

4. Conclusion
Lead has a similar effect on the isothermal surface of the triple indium-tin-vismuth system. At the same time, it should be noted that the maximum surface activity of lead in In-Sn-Bi alloys is somewhat less than that of bismuth in In-Sn-Pi melts. It is shown that with the addition of lead less than 0.1 molar fractions of "depression" on the isothermal surface of the triple system In-Sn-Bi is preserved in the presence of the fourth component (lead). Isothermal surfaces of s are smoothed only at lead content exceeding 0.1 molar fractions.

Thus, we have shown that the increase in the concentration of lead and bismuth in the melt of indium tin-lead-lead-bismuth tends to equalize the peculiarities of the isothermal surface of PN. Nevertheless, with the addition of bismuth to the In-Sn-Pb system, this process is more intensive than with the addition of lead to the In-Sn-Bi system.
Figure 7. Surface tension lines (mJ/m²) in the indium-tin-lead-bismuth system at 623 K and xBi=: a-0.0; b-0.2; in-0.4 mol.

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