Acknowledgment

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Glossary

α, β, δ, A, B, C, D	constants
B_{ii}, B_{ij}	second virial coefficient for pure component and the mixed virial coefficient, respectively
C_1	ternary constant
DEK	diethyl ketone
D, D_{max}	local deviation and maximum local deviation defined by eq 5 and 6, respectively.
m	total number of experimental points
MEK	methyl ethyl ketone
MIBK	methyl isobutyl ketone
n	number of components
P_i°	vapor pressure component i, mmHg
P	total pressure
R	gas constant
t, T	temperature, °C, K
V_i°	molar volume of the pure component
x_i, y_i	mole fraction composition of component i in the liquid and vapor phases
γ_i	activity coefficient
Δx, Δp, Δt	errors in measurements of concentration, pressure, and temperature

Subscripts

calcd	calculated	max	maximum
obsd	observed	i	component i

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Surface Tension and Density of Liquid Tin–Lead Solder Alloys

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As part of the Bureau of Mines program to either conserve scarce domestic mineral resources or substitute for them, development of new soldering systems was undertaken. To support and facilitate this study, the properties of tin–lead solders were investigated. Surface tensions and densities of tin–lead solder alloys have been determined by use of an improved maximum-bubble-pressure system that includes provisions for density measurements. Results show general agreement with accepted theories for simple solutions. Comparisons with other reported measurements on these alloys are made.

Introduction

Over the years many measurements of the surface tensions of tin, lead, and tin–lead alloys have been reported. The results of most of these may be divided into two groups. Some report straight-line temperature–surface tension relationships and show, for binary alloys at constant temperatures, that the relationshsip between the surface tension and composition is represented by concave-upward smooth curves (*5*, *9*, *10*, *23*), in agreement with the accepted theories for simple solutions. Others present curves that deviate from these theories (*1*, *2*, *6*, *7*, *12*, *14*). It is rather interesting that White (*23*), although reporting isotherms that follow accepted theory (*8*, *13*, *19*), shows variable-temperature coefficients for the surface tensions of the binary alloys along with straight-line relationships for the two unalloyed metals. This paper presents data to add to the evidence for normal, simple-solution behavior for surface tension and density of the tin–lead alloys. These data are important becase the general theories of spontaneous wetting and spreading do not agree with the surface tension data for tin–lead solders. Because tin and lead form a simple eutectic system, minimum surface tension, maximum wetting and spreading, and deviations in other properties may be expected to occur at the approximately 63 wt % tin–37 wt % lead eutectic alloy. In actual soldering tests a 50–50 wt % tin–lead alloy spontaneously wets and spreads best (*11*), while the surface tension is lowest for 100% lead and rises according to theories for ideal or simple solutions to a maximum at 100% tin.

The problems of measuring the surface tensions of molten metals are extensive and complicated. The data obtained by others that deviate from simple solution theory may be correct—we cannot judge this —but theory and data should be consistent. This in not true for some of the reported observations. That complete miscibility exists above the liquidus of simple binary eutectic systems, such as tin and lead, cannot be denied, so we prefer to stay with the theory. The data obtained from the improved maximum-bubble-pressure (MBP) system (*17*) have been consistent and reproducible. Several of the researchers who have reported curves that deviate from solution theory relied on sessile-drop or contact-angle systems for determining the surface tension. It is felt that, in light of the anomalous wetting and spreading properties of tin–lead solders, the method of surface tension measurement may enter into the deviations shown. Some of these problems have been reiterated by White in his two reviews on this subject (*21*, *22*) and were illustrated rather vividly by Wilkinson in his review of the surface properties of mercury (*24*).

Experimental Procedure

All measurements were made with an improved maximum-bubble-pressure system which has been described in detail (*17*). This system used a modified form of the Sugden twin-capillary method (*18*), where two capillaries of different radii are placed side by side at exactly the same depth in the liquid.

Table I. Linear Equations for Density of Tin, Lead, and Tin-Lead Alloys

alloy, atomic %	density,[a] g/cm^3	standard error, g/cm^3	temp range, °C
100 Sn/0 Pb	$7.16 - 6.3 \times 10^{-4}T$	±0.012	236-583
73.2 Sn/26.8 Pb	$8.14 - 9.4 \times 10^{-4}T$	±0.12	223-526
60.4 Sn/39.6 Pb	$8.59 - 7.2 \times 10^{-4}T$	±0.12	298-528
43.4 Sn/56.6 Pb	$9.58 - 13.0 \times 10^{-4}T$	±0.22	258-584
30.0 Sn/70.0 Pb	$10.02 - 12.7 \times 10^{-4}T$	±0.20	278-552
0 Sn/100 Pb	$11.13 - 14.0 \times 10^{-4}T$	±0.056	384-551

[a] T in °C.

Table II. Linear Equations for Surface Tension of Tin, Lead, and Tin-Lead Alloys

alloy, atomic %	surface tension,[a] erg/cm^2	standard error, ergs/cm^2	temp range, °C
100 Sn/0 Pb	$566.84 - 4.76 \times 10^{-2}T$	±1.9	240-844
73.2 Sn/26.8 Pb	$516.3 - 5.3 \times 10^{-2}T$	±7.0	195-570
60.4 Sn/39.6 Pb	$498.1 - 4.5 \times 10^{-2}T$	±1.9	211-568
43.4 Sn/56.6 Pb	$489.2 - 6.6 \times 10^{-2}T$	±3.0	269-530
30.0 Sn/70.0 Pb	$478.4 - 6.3 \times 10^{-2}T$	±5.0	297-498
0 Sn/100 Pb	$467.7 - 6.6 \times 10^{-2}T$	±2.1	344-652

[a] T in °C.

The original Sugden method used concentric capillaries. The twin-tube system overcomes the very difficult experimental problem of determining the exact depth of immersion of the capillaries.

Other features of this MBP system included silica capillary tips that are gound internally in a cone shape so that a sharp edge is formed at the periphery (for nonwetting liquid metals, the sharp edge on the outside of the capillary tip assures that the bubbles form and detach at the outside diameter of the tube tip), electronic differential pressure transducers with a digital readout to 0.005 Torr (0.67 Pa), a micrometer screw reading to 0.0001 in. (0.0254 nm) for adjusting the depth of immersion of the capillaries, which permits measurements of both density and surface tension, and a fast-response graphic recorder to monitor the pressure attained for each bubble. Monitoring of bubble formation was also accomplished with contact microphones attached to each gas tube so that bubble detachment could be determined aurally. The gas used to form the bubbles was certified high-purity helium further purified by passing it through a 2-m column filled with heated titanium chips to remove any last traces of oxygen. In every case, the open surface of the molten alloys remained bright and clean during the tests.

Different sets of capillaries were used for the tin, lead, and each of the four tin-lead alloys used in the apparatus. Capillary sizes ranged from about 0.5 to 1.0 mm diameter for the smaller and from about 1.0 to 1.9 mm diameter for the larger. In each set, the diameter of the smaller capillary was 50-60% of the diameter of the larger. Such a capillary size relationship yields the most accurate and consistent data according to theory (*18*). The capillary diameters were measured four to six times with a metallograph having a calibrated filar eyepiece, and the average diameter was determined. The pressure transducers were calibrated against a precision mercury servomanometer, and the complete MBP system was further standardized for each set of capillaries by measuring the surface tension of triple-distilled mercury at 25 °C. For this standardization the value for the surface tension of mercury reported by Ziesing (*25*) of 484.9 erg/cm^2 (0.4849 J/m^2) at 25 °C was used. The use of mercury at room temperature for standardizing the MBP system is valid for subsequent measurements at higher temperatures because of the very low coefficient of expansion for silica and because the thermal expansion of each set of two capillary tips is practically self-canceling.

The tin and lead used for the alloys were of 99.999% purity. Spectrographic analyses of the tin showed only trace amounts (10 ppm) of silicon and calcium. Analyses of the lead showed traces of silicon and copper as detectable impurities. Analyses were made before and after surface tension and density were measured. All procedures necessary for handling high-purity metals were observed. However, the MBP method tends to minimize the influence of surface-active impurities (*3*); therefore, the purity of the molten metals and alloys tested was not considered a major factor in the accuracy of the results presented. The compositions of the alloys given in Table I and II are from analyses of the alloys used.

Corrections for the nonsphericity of the bubbles resulting from the pressure head of the liquid metal above the tips were made by the method proposed by Sugden (*18*). A summary of Sugden's method is also given by White (*21*, *22*). The correction method involves a comprehensive series of successive approximations, so a digital computer was used to reduce the raw data and derive the value for surface tension and density.

Temperatures in the melt were measured using a Type K thermocouple in a silica protection tube positioned in close proximity to the capillary tips. The charge was about 0.5-0.8 kg and was contained in a silica crucible. The densities measured were used in the calculations for the surface tension values. Slight changes in liquid level in the crucible resulting from the changes in the immersion of the capillaries and the thermocouple tube were calculated from the dimensions of these parts and the crucible. These corrections for changes in liquid level were included in the calculation for density. They do not affect the surface tension results.

Results

Density. The equations for density were obtained from linear least-squares analyses of the experimental data and are given in Table I for the two metals reported on before (*15*, *16*) and the four solder alloys. Standard errors of the data about the predicted values of density are also shown, along with the temperature ranges over which the density measurements were made. Figure 1 shows the straight-line plots of density vs. temperature for tin, lead, and each of the tin-lead alloys. Experimental data for the alloys are located along the straight lines. Each of these points represents the average of from 4 to 12 experimental measurements at the particular temperature involved. The data for tin and lead are from the previous publications noted (*15*, *16*).

In Figure 2 the 350 °C isotherms of density vs. tin-lead composition are shown for this work and that of Arpi (*4*) and Thresh, Crawley, and White (*20*). The 350 °C isotherm is often

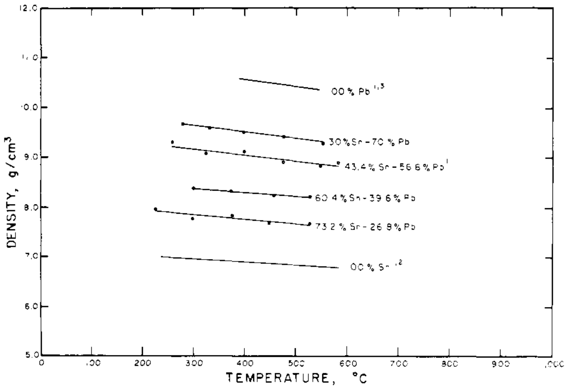

Figure 1. Density vs. temperature for tin, lead, and tin-lead alloys (compositions in atomic percent).

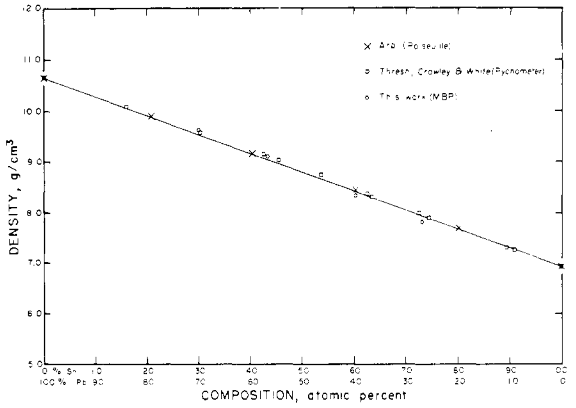

Figure 2. Density vs. composition for tin, lead, and tin-lead alloys at 350 °C (isotherm).

used for measurements on tin-lead alloys because it represents approximately 25 °C superheat over the maximum liquidus of the Sn-Pb system. The data points plotted for the present work were calculated from the equations listed in Table I. A straight line drawn through the points indicates the excellent agreement of the data points among the three different sets of density data.

Surface Tension. Equations derived from a linear least-squares analysis of the experimental surface tension data are shown in Table II for tin, lead, and the four tin-lead alloys investigated. Also listed are the standard errors for the data about the predicted values of surface tension for each equation and the temperature range over which the experimental measurements were made. Graphical presentations of the straight lines representing the surface tension equations given in Table II are shown in Figure 3. Also shown for the tin-lead alloys are experimental data points from which each of the straight-line equations were derived. Each of these points represents an average of two or more measured values. Again, the values for tin and lead are from previous publications (*15*, *16*).

Tables 3, 4, 5, and 6 (not published here) give the experimental and calculated data for each temperature indicated in Figures 1 and 3. These data are available as supplementary material.

In Figure 4, the 350 °C isotherms of the composition vs. surface tension for this work and those for that of several others are plotted for comparison. Although many more sources of data (*1*, *2*, *7*, *12*, *14*) are cited above than are shown in the figure, all are not included because they deviate noticeably from the curves shown and would only add confusion. Values for this work are calculated from the equations shown in Table II. For the other surface tension data on the graph, Bircumshaw (*5*) used the maximum-bubble-pressure method, Coffman and Parr (*6*) used the drop weight method, White (23) used the sessile drop method, and Hoar and Melford (*10*) used the capillary rise method. On the high-tin side of the graph, the data from the present work lie between those of Hoar and Melford and those of White and of Bircumshaw. Coffman and Parr's data are much lower on the tin side and exhibit an erratic behavior for lower tin contents. Surface tension values given by Hoar and Melford become increasingly higher as tin content is decreased until at 100% lead their values are as much as 35 erg/cm^2 higher than other data presented. On the high-lead side of the graph, surface tensions from the present work agree closely with most of the others listed. The isotherm for this work exhibits a smooth quadratic curve which obeys the following equation to within 0.5%

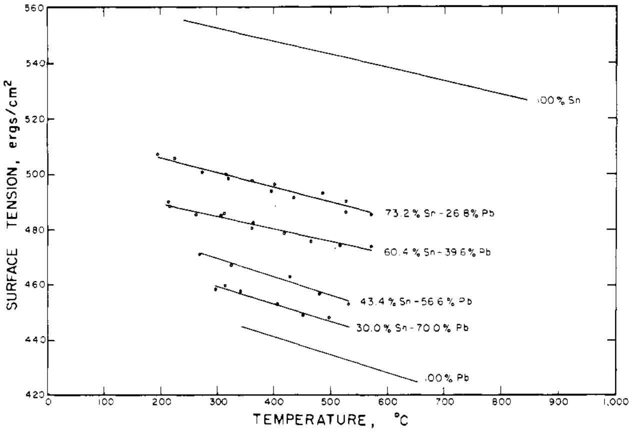

Figure 3. Surface tension vs. temperature for tin, lead, and tin-lead alloys (compositions in atomic percent).

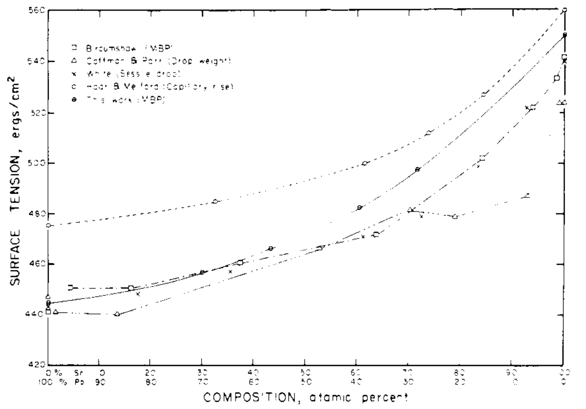

Figure 4. Surface tension vs. composition for tin, lead, and tin-lead alloys at 350 °C (isotherm).

$$\gamma = 445.7 + 0.0117C + 0.0102C^2$$

where γ is the surface tension in erg/cm^2 and C represents the tin composition in atomic percent. Adamson (*3*) states that, in general, for binary systems in which the two components have similar surface tensions and the system behaves as a regular solution, their surface tension can be expressed or predicted as follows:

$$\gamma_{\text{mix}} = \gamma_1 N_1 + \gamma_2 N_2 - \beta N_1 N_2$$

where γ_1 and γ_2 are the surface tension of the respective pure liquids, N_1 and N_2 are their mole fractions, and β is a semiempirical constant. When using our experimental values for surface tension of tin and lead in the equation, and a point on the 350 °C isotherm in order to calculate β, the predicted values of surface tension from the equation are within 0.5% of any taken from the isotherm shown. Isotherms drawn at other temperatures yielded the same type curves for the surface tension data presented in this report. The authors believe that these smooth isotherms are appropriate and reflect the precision of surface tension measurements made on the tin, lead, and the four tin–lead alloys.

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Supplementary Material Available: Tables 3, 4, 5, and 6, surface tension and density data for *xx* Sn/*xx* Pb (3 pages). Ordering information is given on any current masthead page.

Liquid–Vapor Equilibria at 270.00 K for Systems Containing Nitrogen, Methane, and Carbon Dioxide

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Liquid–vapor equilibria for the binary systems nitrogen–carbon dioxide and methane–carbon dioxide and for the ternary system nitrogen–methane–carbon dioxide were measured at 270.00 K and at pressures of 32–122 atm.

Introduction

Recent industrial interest in the low-temperature high-pressure processing of hydrocarbons has increased the need for reliable data on the components found in natural gas. The objective of the work reported here was to provide accurate experimental measurements on a system of industrial interest and to assess the feasibility of modeling the phase equilibria with a simple two-parameter equation of state.

The experimental work involved the binary systems methane + carbon dioxide and nitrogen + carbon dioxide and the ternary system methane + nitrogen + carbon dioxide. There are experimental data available in the literature for the binaries of nitrogen, methane, and carbon dioxide, but there is only one measurement on the ternary system. Previous experimental work prior to 1973 has been reported by Hiza, Kidnay, and Miller (*4*). Table I summarizes all the recent work not covered in ref 1.

The equations of state chosen for study were the equation of Redlich and Kwong in the modified forms proposed by Prausnitz (*12*, *13*), Soave (*17*), and Chaudron et al. (*2*) and a modified van der Waals equation proposed by Peng and Robinson (*10*).

Experimental Equipment and Procedure

A schematic of the experimental apparatus is shown in Figure 1.

The cryostat was a stainless-steel dewar having a 27-L capacity. The constant temperature bath fluid was a 50 vol % mixture of carbon tetrachloride (CCl_4) and chloroform ($CHCl_3$). Suspended in the bath was the stainless-steel equilibrium cell, a refrigeration coil where ethylene glycol was circulated as a cooling fluid, two heaters where one had a proportional controller, a two-propeller mixer with variable speed, and a calibrated (IPTS-68) platinum resistance thermometer. Vapor circulation in the loop was obtained with a high-pressure diaphragm pump. The vapor from the pump passed through a heat exchanger in the bath fluid before entering the equilibrium cell. Liquid samples were withdrawn from the equilibrium cell through a capillary line.

Table I. Summary of Data Not Reported by Hiza, Kidnay, and Miller (*4*)

system	temp range, K	pressure range, atm	citation
$CH_4 + CO_2$	253, 273, 288	26–84	1
$CH_4 + CO_2$	230, 250, 270	9–85	3
$CH_4 + CO_2$	153–219	12–64	5
$CH_4 + CO_2$	153, 173, 203, 210, 183, 193, 219	6–64	8
$N_2 + CO_2$	253, 273, 288	20–150	1
$N_2 + CH_4$	112, 120, 130, 140, 150, 160, 170, 180	1–50	6
$N_2 + CH_4 + CO_2$	233, 253, 273	60, 80, 100	15

The temperature was measured to ±0.02 K using the calibrated (IPTS-68) platinum-resistance thermometer connected to a Mueller bridge and a null detector. The temperature control was maintained by using a 1700-W immersion heater driven by a power proportioning controller with a tested sensitivity of ±0.001 K. To eliminate temperature gradients, a variable-speed, two-propeller stirrer was constantly on.

The pressure measurement was made with one of two Heise gauges, a 0–100 atm or a 0–2000 psia gauge, which were calibrated against dead weight testers. Average deviations of ±0.015 atm and –1.6 psi were measured for the two gauges, respectively, over the pressure regions of interest.

A gas chromatograph equipped with a thermal conductivity detector and a 6 ft, 60/80 mesh silica gel column was used in the analysis. The chromatograph conditions were adjusted to obtain very sharp, symmetric peaks, and these peak heights

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