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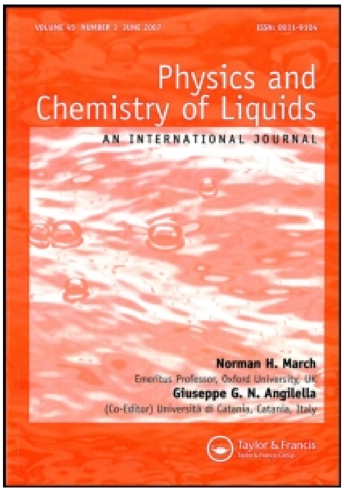

Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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F. A. Kanda[a]; R. P. Colburn[a]
[a] Department of Chemistry, Syracuse University, Syracuse, New York

To cite this Article Kanda, F. A. and Colburn, R. P.(1968) 'The Absolute Viscosity of Some Lead-Tin Alloys', Physics and Chemistry of Liquids, 1: 2, 159 — 170

To link to this Article: DOI: 10.1080/00319106808083795

URL: http://dx.doi.org/10.1080/00319106808083795

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Physics and Chemistry of Liquids. 1968. Vol. 1, pp. 159–169

Printed in Great Britain

The Absolute Viscosity of Some Lead-Tin Alloys

F. A. KANDA and R. P. COLBURN

Department of Chemistry
Syracuse University
Syracuse, New York

Received July 1, 1968

Abstract—The absolute viscosity of lead, tin and nine of their alloys were measured as a function of temperature between the liquidus and 500°C by an oscillating cup viscometer. The viscosity of pure tin ranged from 0.01780 poise at 235°C to 0.01196 poise at 458°C. The viscosity of pure lead ranged from 0.02578 poise at 334°C to 0.01896 poise at 472°C. Viscosity isotherms, as a function of composition, showed an ideal linear behavior with no anomaly detected at the eutectic composition (26.1 at % Pb). A plot of $\log \eta$ versus $1/T$ was linear for all samples. Accuracy of the data is estimated to be about 1%.

Introduction

In the determination of the viscosity of pure lead and tin, as a function of temperature, a number of authors have reported widely differing values.[1–9] This disagreement has been particularly pronounced in the case of tin. Several of these authors have also studied the viscosity of lead–tin alloys as a function of composition. Their reported values likewise display large disparities.[1–5] However, their results contain a common feature consisting of a relative viscosity minimum at the eutectic composition (73.9 at. % Sn). The magnitude of this anomaly varies among the results of different reports. Some authors cite, as a possible explanation for this minimum, short range order effects in the melt[1,3,4] with "competition between phases"[3] occurring at the eutectic composition. Gebhart and Kostlin,[6] using a calibrated oscillating cup viscometer, found no anomaly at this composition. They found a smooth, relatively ideal behavior for the viscosity–composition isotherms. In view of the discrepancies in the literature values, it was felt that a careful study of viscosity, as a function of temperature and composition for the lead–tin alloy system by an absolute method, and using very pure metals would be useful.

Apparatus

The oscillating cup viscometer used for this work is similar in construction and operation to the apparatus described by Thresh.[7]

The viscometer is illustrated schematically in Fig. 1. It consists of a precision machined graphite cup (*L*) threaded on to a graphite over-flow reservoir (*J*) which acts as a cap. This cap is attached to a stainless steel tube (*I*) by means of another threaded graphite piece. The tube extends out of the furnace region (*M*) passing through holes located in the centers of a set of stainless steel radiation shields (*X*). The tube passes axially through an inertia ring and ring holder (*W*) which is attached to the tube and held concentric about the axis of oscillation by means of set screws.

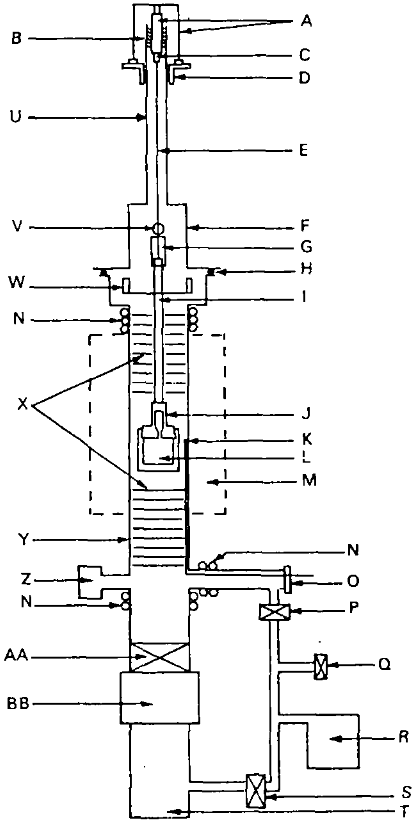

Fig. 1. Oscillating cup viscometer.

Above the inertia ring the steel tube is fastened to the pulley housing (*G*). The pulley housing contains a stainless steel wheel with a shallow groove cut around its perimeter. The groove positions a 0.004″ diameter tungsten wire bifilar suspension (*E*) which is slung around the wheel. The suspension wires pass up out of the pulley housing past either side of a mirror (*V*) fastened to the top of the pulley housing. The wire extends about 1 meter above the wheel to the suspension grips (*C*) which holds the wire with set screws. The suspension grips are attached to the support head (*A*) which extends up out of the brass chamber (*U*) through a vacuum tight o-ring seal (*B*). The support head allows the application of a twisting motion to initiate a torsional oscillation of the pendulum. The vacuum system allows the apparatus to be evacuated to a pressure of less than 10^{-6} torr. The furnace has three individually controlled zones. The sample cup lies at the center of the central zone. Four thermocouples are positioned above, below and beside the graphite cup.

The photographic recording system is illustrated in Fig. 2. A light source and lens focusing system (*A*′) is aimed to reflect from the mirror

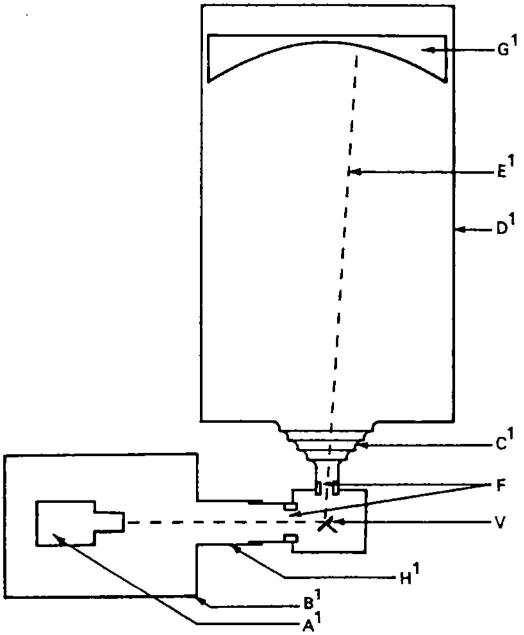

Fig. 2. Photographic recording system.

(V) and project a focused line image 0.4 mm wide on a 35 mm film in the film holder (G'). The film holder is located 1 meter from the mirror and is bent to a 1 meter radius of curvature to keep the image in sharp focus and avoid the need for a $\tan\theta$ to θ correction required of a flat scale.

The metals used in this work were obtained from the United Mineral and Chemical Corp. and reported by the supplier to be 99.999 % pure. After the alloys had been cast and run, a sample was sent to the National Spectrographic Laboratory, Cleveland, Ohio, for analysis of trace impurities. They checked for and were unable to detect the following elements: Ag, Al, As, B, Ba, Bi, Ca, Cb, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Sb, Si, Sr, Ti, V, W, Zn, Zr. No elements other than lead and tin were detected.

The alloys were cast in a graphite mold under an argon atmosphere. They were thoroughly stirred with a plunger and rapidly cooled to minimize segregation upon solidification. The casting was machined to dimensions which would allow for thermal expansion of the solid ingot without breaking the viscometer graphite cup during heating, but large enough to completely fill the sample cup upon melting. The sample cup containing the machined casting was put under vacuum, 10^{-6} torr., and brought to the desired temperature. As the liquid metal expanded and finally filled the cup, the excess material was forced through a 0.05″ hole in the base of the over-flow reservoir (J). This excess liquid was prevented from contributing to the viscous drag by a set of vertical graphite baffle plates which were held submerged by a tungsten weight. These baffle plates also act as a one way valve. After the final run was made at the maximum temperature the furnace was shut off. As the cooling liquid began to contract the baffle plates covered the hole at the base of the reservoir and the liquid present at the maximum temperature of the experiment was trapped. Thus weighing the ingot remaining in the cup at room temperature permitted an accurate determination of the density of the melt at the maximum temperature achieved in the investigation, since the volume of the cup at this temperature is also known.

During an experimental run the sample was thermally equilibrated for 3 to 4 hours. Then the cup was given a torsional oscillation and the decaying amplitudes were recorded on film as a series of fine lines. The light intensity was adjusted so that only the end points of the swing, where the image comes to a momentary rest, developed on the film.

The absolute viscosities were obtained from the experimental data using the equations developed by Roscoe for the closed oscillating cylindrical cup viscometer.[10]

$$\eta = \left[\frac{I\delta}{2\pi R^3 H Z}\right]^2 \frac{1}{\pi T \rho}$$

where:

$$Z = \left(1+\frac{1}{4}\frac{R}{H}\right)a_0 - \left(\frac{3}{2}+\frac{4}{\pi}\frac{R}{H}\right)\frac{1}{p} + \left(\frac{3}{8}+\frac{9}{4}\frac{R}{H}\right)\frac{a_2}{2p^2}$$

$$p = \left(\frac{\pi\rho}{\eta_{\text{est}} T}\right)^{1/2} R$$

$$a_0 = 1-\frac{1}{2}\Delta-\frac{3}{8}\Delta^2;\quad a_2 = 1+\frac{1}{2}\Delta+\frac{1}{8}\Delta^2;\quad \Delta = \frac{\delta}{2\pi}.$$

I is the moment of inertia of the oscillating system, δ is the logarithmic decrement, R is the radius of the cup, H is one-half the height of the cup, T is the period of oscillation, ρ is the density of the fluid, a_0, a_2 and Δ are theoretical parameters obtained from the logarithmic decrement and η_{est} is an estimated viscosity used in the calculation of P which is used to calculate Z and finally η. This new value of η was then substituted for η_{est} and the process repeated until the approximations converged to the desired accuracy.

The viscosities of pure lead and tin and nine of their alloys were determined at temperatures ranging from the liquidus to 500°C. Plots of the logarithms of the viscosities versus $1/T$°K are shown in Figs. 3 and 4. Interpolations from these linear plots were used to construct the viscosity isotherms as a function of composition shown in Fig. 5. The viscosities are given in tabular form in Table 1. The densities used in the calculation of these viscosities are included to facilitate comparison with other published viscosity values.

Due to segregation on solidification of the casting and the subsequent machining of the sample, the final composition could not be assumed to be the same as the make up composition. Chemical analysis of the total sample following a run was impractical due to its relatively massive size (250 to 350 gm). Also chemical analysis of a representative portion of the sample was not possible due to segregation on solidification. However, accurate density values representative of the entire liquid sample were obtained for each alloy at the maximum temperature of the viscosity determinations (circa 500°C). Density values obtained by this technique

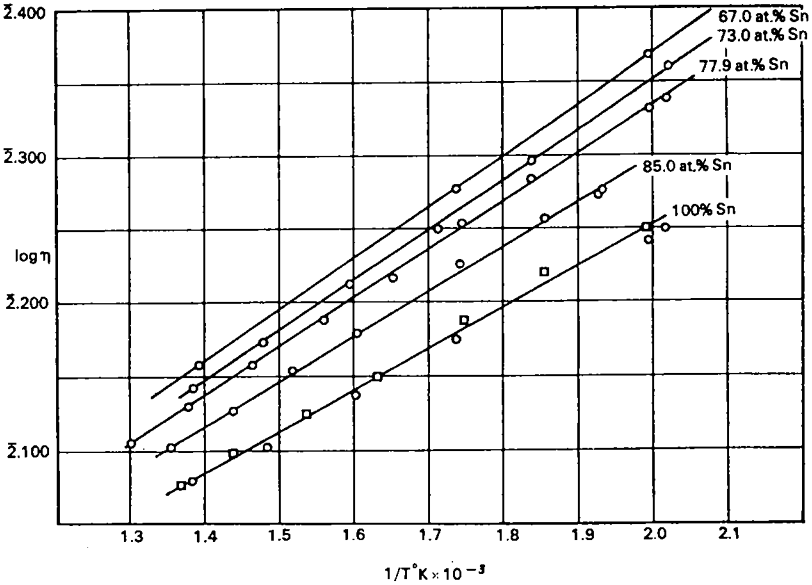

Figure 3

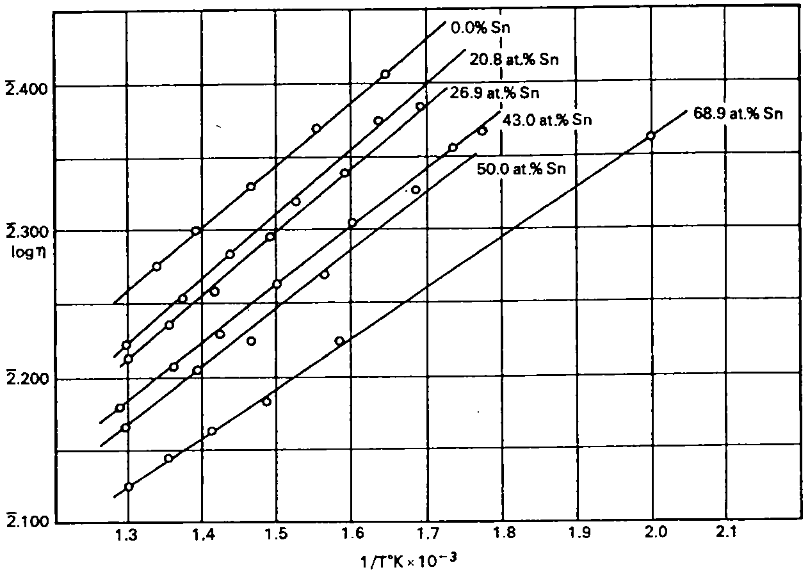

Figure 4

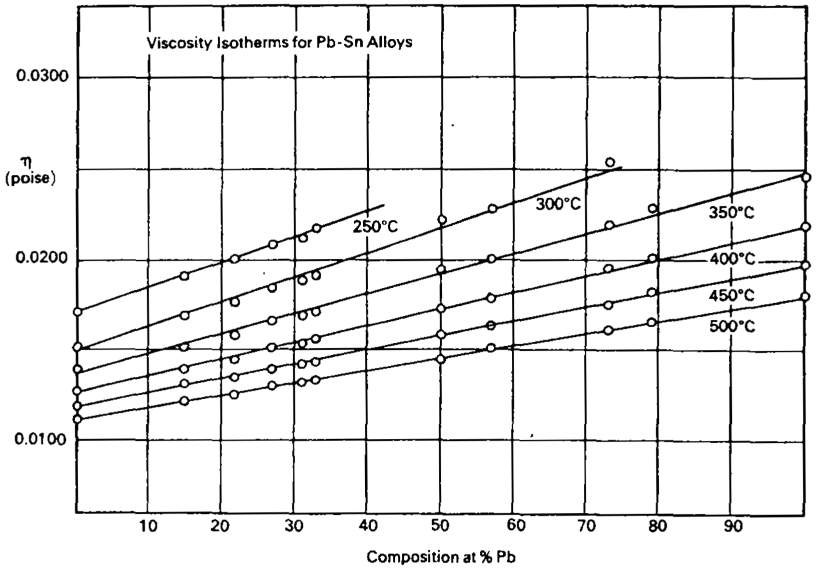

Figure 5

for pure tin at 450°C and 492°C were 6.821 gm/cm^3 and 6.798 gm/cm^3 respectively and for pure lead at 472°C was 10.487 gm/cm^3. These are in excellent agreement with current literature values.[1,7] Fisher and Phillips state that the composition–density relationship for the lead–tin alloy system is almost linearly ideal, especially at higher temperatures.[1] Therefore, alloy compositions were assigned on the basis of density assuming a linear density–composition relationship. The coefficients of expansion for the liquid alloys were taken as the weighted mean of the pure components.

The activation energies for viscous flow, as determined from the slopes of the log η versus $1/T$°K plots, are shown in Table 2.

The estimated uncertainty in the values of the parameters used to calculate the viscosity are listed in Table 3. The probable errors are expressed in terms of the actual quantity measured (σ_A) and as a percentage uncertainty in the viscosity caused by the parameter error (σ_B). In the case of I, T, δ, R, and H the estimates are based on the precision of repeated measurements. In the case of ρ and temperature the estimates were more difficult to assess. For density, the assumed ideal composition–density relationship and ideal coefficient of thermal expansion may

TABLE 1

Temp. (C)	ρ (gm/cm^3)	η (poise)
	100.0 at % Sn	
235	6.990	0.01780
241	6.985	0.01741
266	6.964	0.01658
299	6.943	0.01541
303	6.942	0.01498
340	6.914	0.01426
351	6.907	0.01373
378	6.886	0.01337
401	6.870	0.01267
422	6.854	0.01254
450	6.821	0.01198
458	6.835	0.01196
	85.0 at. % Sn	
244	7.510	0.01945
246	7.510	0.01930
266	7.490	0.01814
301	7.460	0.01687
350	7.435	0.01514
386	7.400	0.01427
422	7.375	0.01338
466	7.345	0.01267
	77.9 at. % Sn	
222	7.800	0.02179
228	7.795	0.02149
271	7.760	0.01928
300	7.750	0.01794
332	7.730	0.01648
368	7.705	0.01541
410	7.680	0.01438
453	7.650	0.01349
496	7.620	0.01270
	73.0 at. % Sn	
221	7.990	0.02292
272	7.960	0.01982
311	7.930	0.01804
354	7.900	0.01635
403	7.850	0.01488
449	7.810	0.01384
496	7.755	0.01302
	68.9 at. % Sn	
226	8.160	0.02306
357	8.030	0.01681
399	8.000	0.01530
435	7.970	0.01464
465	7.950	0.01395
499	7.920	0.01333
	67.0 at. % Sn	
228	8.230	0.02318
303	8.140	0.01899
446	8.035	0.01438
	50.0 at. % Sn	
290	8.830	0.02333
322	8.790	0.02134
366	8.750	0.01869
408	8.715	0.01686
446	8.675	0.01588
498	8.615	0.01469
	43.0 at % Sn	
303	9.040	0.02273
351	9.025	0.02017
393	8.990	0.01831
428	8.975	0.01693
461	8.925	0.01611
502	8.835	0.01517
	26.9 at. % Sn	
319	9.650	0.02426
355	9.625	0.02195
396	9.570	0.01977
433	9.530	0.01815
463	9.485	0.01724
496	9.455	0.01636
	20.8 at. % Sn	
338	9.875	0.02379
382	9.825	0.02097
422	9.775	0.01922
454	9.750	0.01801
498	9.690	0.01674
	100 at. % Pb	
334	10.69	0.02578
370	10.64	0.02346
408	10.58	0.02141
444	10.53	0.01995
472	10.49	0.01896

TABLE 2

Composition (at. % Sn)	Activation Energy for Viscous Flow (kcal/gm atom)
100.0	1.4
85.0	1.5
77.9	1.5
73.0	1.6
68.9	1.5
67.0	1.6
50.0	1.8
43.0	1.8
26.9	2.0
20.8	2.1
0.0	2.0

TABLE 3

	Parameter	σ_A	σ_B	σ_B^2
I	Moment of Inertia	8 gm cm^2	0.4	0.16
T	Peroid of Oscillation	0.01 sec	0.1	0.01
δ	Logarithmic Decrement	0.00009	0.6	0.36
R	Radius of Cup	0.0005 cm	0.3	0.09
H	Half Height of Cup	0.0005 cm	0.1	0.01
ρ	Density	0.5%	0.5	0.25
			$\sum\sigma_B^2 =$	1.13

$$\sigma_\eta \simeq (\sum\sigma_B^2)^{1/2} \simeq 1.1\%$$

warrant the estimate of 0.5% error in the viscosity. The agreement of the density measurements for pure tin and lead with literature values are in the order of 0.2%.[1,7] The estimate of the temperature error is probably too high but the experimental situation did not permit contact of the thermocouples with the sample. The thermocouples were approximately 1/8″ from the cup under high vacuum. They indicated a melting point for 99.999% tin of 233°C (231.7°C is standard) as determined by the onset of liquid damping of the pendulum during a very slow heating rate. An error of 2°C would cause a viscosity error of about 0.5% for these alloys. The total uncertainty in the viscosity is about 1%.

When accurate experimental data are available for the density–

composition relationship for these alloys, a refinement of the present viscosity data can be made. However, it is unlikely that this will affect the results by more than a fraction of 1 %

The viscosity of mercury is probably the best established of any liquid metal.[14] Therefore, as an additional check of the apparatus the viscosity of triply-distilled mercury was measured at 20.0°C. The value : $\eta = 0.01551$ poise, was obtained using a density of 13.545 gm cm^3. This viscosity value agrees with the results of Erk[15] and Menz and Sauerwald[9] to within 0.5%.

Recent viscosity determinations have been made on several pure metals by Menz and Sauerwald[9] using a capillary method. From their work and other current literature values, they express a viscosity–temperature relationship for lead as: $\log \eta = 0.4401 \times 10^3/T - 0.3134$ and for tin as: $\log \eta = 0.3044 \times 10^3/T - 0.3396$, where η is expressed in centipoise and T in degrees Kelvin. These equations are plotted in Fig. 6 along with the experimental results of this paper. The agreement is good to within about 1%. The present viscosity values for tin are about 10% below those of Fisher and Phillips.[1] It should be noted that three of their five calibration points were based on assumed viscosity values for tin at three different temperatures. Gebhart and Kostlin[6] used the data of Bienias and Sauerwald[12] and Landdolt–Bornstein[13] to establish their apparatus constant.

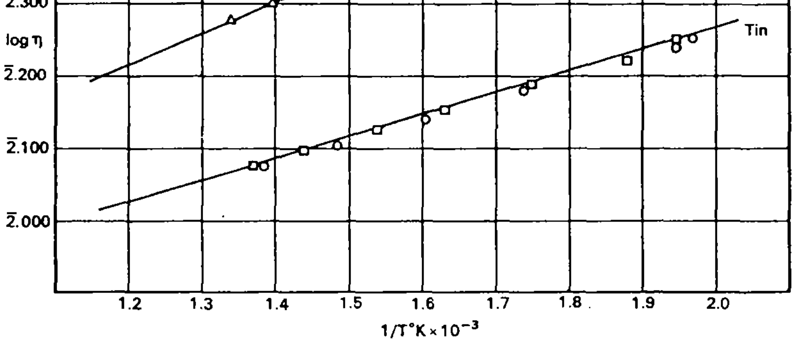

Figure 6

Our absolute viscosity values are below those of Gebhart and Kostlin but they observed no anomaly at the eutectic composition, which is in agreement with the present work.

The absence of a viscosity minimum at the eutectic composition is in marked contrast with the findings of several previous reports.[1,2,3,4] Recent work by Adams and Leach,[11] measuring resistivity–composition isotherms for the lead–tin system, reveal no anomalous behavior at the eutectic composition, although the work of Toye and Jones does.[3] Adams reports considerable nonhomogeneity in the liquid alloy samples unless great care was taken to assure uniformity by mechanical mixing. This agrees with our early experience in attempting to cast alloy samples by induction heating without mechanical mixing. It may be possible that the reported viscosity anomalies in the region of the eutectic are the result of incomplete mixing of the alloy.

The present work finds no evidence to support pre-freezing clustering effects in either pure metal investigated. The linear viscosity–composition isotherms offer no evidence for the existence of a "quasi-eutectic structure" in the liquid alloys.

Acknowledgement

The authors wish to acknowledge grateful thanks to their machinist Mr. James Fisher for his accurate work in the construction of the viscometer components and to the A.E.C. for their financial assistance with this project.

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