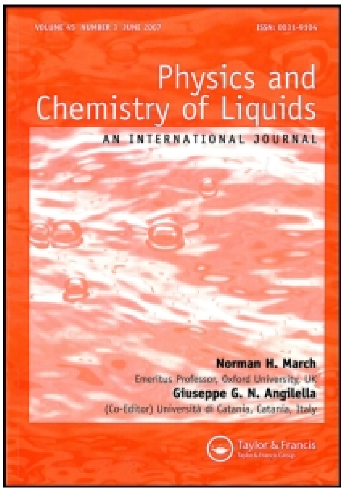

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Volume Change on Formation and Thermal Expansion Coefficient of Liquid Hg-In Alloys

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Abstract—The volume change on formation of liquid mercury–indium alloys has been precisely measured at 162°C for eleven compositions. The thermal expansion coefficient of the liquid alloys between 20° and 160°C was measured at compositions up to 70 at. % indium. The composition dependences of the density and of the thermal expansion coefficient are discussed and compared with the composition dependences of other physical properties of these alloys.

Introduction

The electrical and galvanomagnetic properties of liquid amalgams have recently been the object of several investigations.[1,2] For pure mercury and the other components of the alloys the Hall coefficient in the liquid state indicates a number of current carriers equal to the valence electron concentration,[3] the alloys however show departures from the weighted mean values.[4] The optical properties show similar departures from the expected behaviour.[5] The resistivity of mercury falls markedly on alloying, almost irrespective of the alloying component.[6] Despite substantial departures from Vegard's Law the heats of mixing of many amalgams are surprisingly small.[7]

In order to relate on an atomic basis the properties of the alloys with those of the components, precise data on the density of the alloys over a range of temperatures are required. This paper describes the results of measurements of the volume change on formation, and of the expansion coefficient, for several liquid mercury–indium alloys.

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Experimental Methods

The excess molar volume was determined as a function of composition at one temperature using a modified version of a previously published dilatometric technique.[8] The expansion coefficient was determined for selected alloys over a range of temperature by standard pyknometry.

The excess volume of mixing was measured directly by observing the decrease in volume on mixing the liquid components. The two metals were contained in separate arms of a "U" tube and covered with a dilatometric fluid, the level of the meniscus being observed in a calibrated capillary which extended out of a thermostat. The capillary and "U" tube were so arranged that by tilting the capillary the metals would mix and flow into one arm of the "U" tube. Serious errors may arise when using this technique from chemical instability of the dilatometric fluid, thermal instability of the environment and degassing of the materials and container.

A *silicone oil* (DP 190 from I.C.I.) was used as the dilatometric fluid. This was found to be more stable than a mineral oil as used in the previous work and proved satisfactory in contact with the alloys up to 200°C. It had the advantages of low volatility and it prevented wetting of the glass cell by the liquid indium. However, its high viscosity necessitated warming the capillary before the mixing operation, since the speed of the reaction, which produced a contraction, otherwise caused the thread of fluid in the capillary to break.

The mean temperature of the thermal environment was controlled to ± 0.01°C. This was achieved in a thermostat bath which was well-insulated and contained 6 litres of oil. The bath heating coil was placed remote from the mixing cell, and the bath was vigorously stirred from the center of this coil. The sensing element of the thermostat control was a platinum resistance thermometer placed near the heating coil. The temperature was measured to ± 0.1°C by a calibrated chromel–alumel thermocouple attached to the mixing cell.

Degassing the metals, glassware and dilatometric fluid was necessary to prevent bubble formation within the cell. The components of the alloy were heated above their melting points in the cell under vacuum, and the cell was then filled under vacuum with hot silicone oil.

The measurements were made by observing the meniscus level in the capillary with a cathetometer for 20 minutes prior to mixing the metals. After mixing, time was required for the system to homogenise and allow the heat of mixing to be dissipated. The meniscus level was then observed for a further 20 minutes. A typical variation of meniscus level as a function of time is shown in Fig. 1. This represents a steady drift of the meniscus level on which are superimposed changes arising from the thermal fluctuations of the thermostat. The cell behaves as a sensitive thermometer and fluctuations which correspond with the cycling of the heating current represent variations in temperature of less than ± 0.0125°C. The change in meniscus level due to mixing was obtained by extrapolating the curves to the mixing time. In good conditions this could be measured to ± 0.005 cm. The total change in level using a $\frac{1}{2}$ mm diameter capillary and 0.1 gm

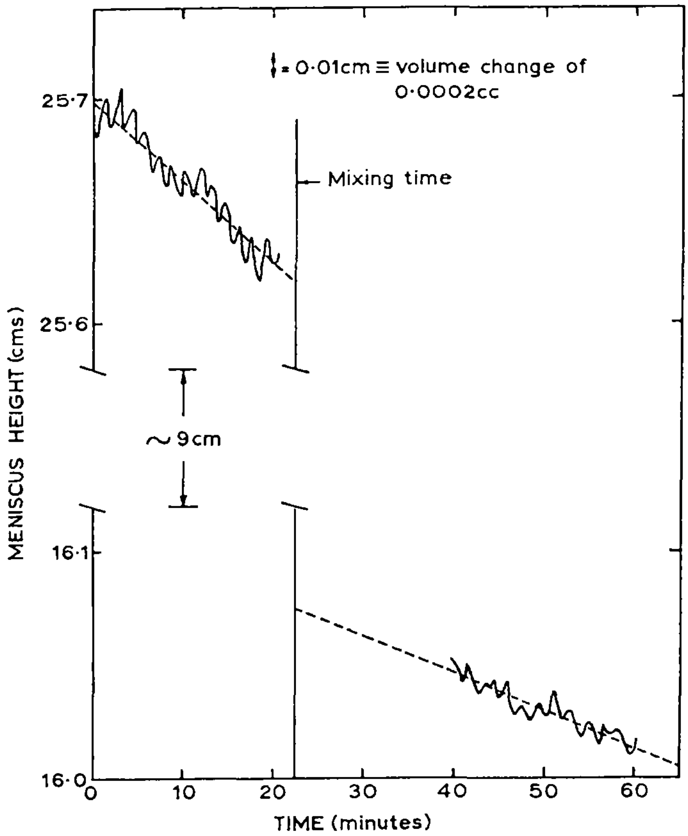

Fig. 1. Typical graph of meniscus level as a function of time

atoms of 50 : 50 alloy, was 10 cm. This magnitude of change in level was maintained, as far as possible, by altering the amount of alloy used.

Results were obtained over the whole composition range, with particular attention to the low indium concentrations, where it had been suggested[1] that there might be irregularities in the density.

The expansion coefficients were measured by a simple pyknometric technique. The pyknometer was a small bulb of about 4 cc volume and a capillary with a narrow exit. This held about 0.25 gm atoms of alloy.

The pyknometer was initially filled under vacuum at a temperature just above the liquidus of the alloy under investigation. It was then immersed, except for the tip of the capillary, in the thermostatic bath. Measurements were made by collecting the alloy expanded out of the bottle, (as the temperature of the bath was increased in steps). These small quantities of exuded alloy were collected and weighed, and the results used to investigate the relation between molar volume and temperature. The pyknometer bottles were also weighed at the beginning and end of the run, and the weight difference, which was determined more accurately than the weight of the exuded alloy, was used to calculate the mean value of the expansion coefficient. The pyknometers were calibrated with mercury, and thus all values are calculated with respect to the coefficient of expansion of mercury.

The most serious problem, as with the volume of mixing experiments, arose from gas evolved from the metal. This was reduced to a minimum by mixing the alloy at high temperature under vacuum, and, in the same operation, cooling and vacuum filling the pyknometer.

Results

The results of the excess volume experiments at 162°C are shown in Fig. 2 as a function of composition. For low indium concentrations the excess volume is nearly a linear function of composition, and the maximum value of 0.26 cc/gm atom occurs near 38% In. The deviation from the smooth curve of 0.003 at 50% In may be a real effect as it is an order of magnitude greater than the experimental error, which is estimated by ±0.0005 cc. Also shown in Fig. 2 are the previously published data, obtained at 158°C, and corrected to 162°C using the values of the expansion coefficient obtained in the present investigation. Table 1 lists the present results, as the precision is greater than can be shown on the graph.

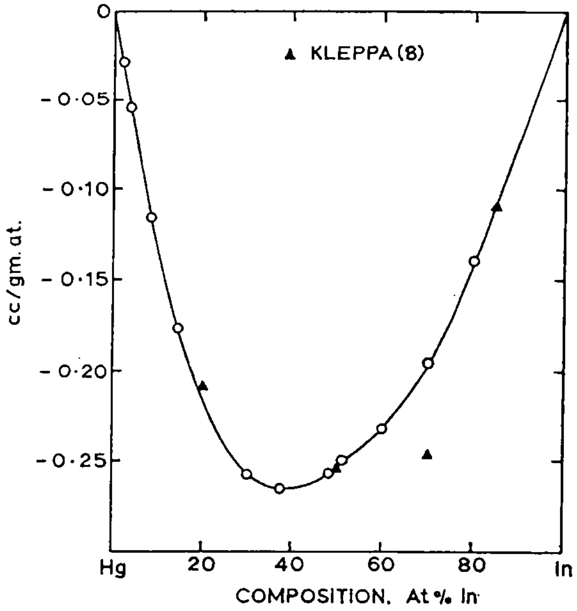

Fig. 2. Volume contraction as a function of composition (at 162°C).

TABLE 1 The volume change on mixing liquid indium and mercury at 162°C

Composition atomic % In	Volume change cc/gm atom
2.02	– 0.0287 ± 0.0005
3.67	– 0.0540
8.33	– 0.1153
14.63	– 0.1765
29.93	– 0.2575
37.69	– 0.2651
48.29	– 0.2574
51.12	– 0.2499
59.98	– 0.2323
70.00	– 0.1955
80.03	– 0.1392

The coefficient of thermal expansion is shown as a function of composition in Fig. 3. The experimental points for molar volume as a function of temperature did not show any significant deviations from linearity. The results are therefore presented as an average value for the expansion coefficient between 20 and 160°C. The value for pure indium is taken from

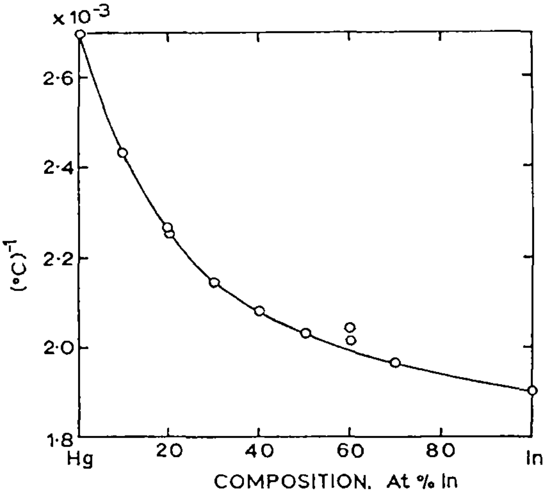

Fig. 3. Thermal expansion coefficient as a function of composition.

the data of Williams and Miller[9] at the melting point, and the value of 2.698 × 10^{-3}/°C for the expansion coefficient of mercury from standard tables.[10] For pure mercury, the expansion is not quite linear, and the value taken is the mean for the range 20–160°C.

The results are estimated to be accurate to ± 1%. While no explanation is currently available for the deviation of the two samples at 60% indium which are off the smooth curve these points are just within the estimated error limits.

Discussion

The excess volume in the Hg–In system is in reasonable agreement with the previous results for mixing the liquid components, except for the rather marked difference at 70% In. Some of the previous results which were obtained at lower temperatures by mixing solid indium and liquid mercury showed much larger inconsistencies. The present results, which are believed to be nearly an order of magnitude more precise, and are more detailed, give no support for the suggestion of density variations which might account for peculiarities in the thermoelectric power.[1]

The expansion coefficient of mercury–indium does not appear to have been measured directly before, except for very dilute amalgams.[11] The present data is based on values of the density of mercury as a function of temperature which are known very accurately. Two sets of data for the density of liquid indium were found. The results of Williams and Miller[9] are some 0.15% higher than those of McGonigal, Cahill and Kirshenbaum[12] but the earlier results are preferred as the expansion coefficient ($1.9 \times 10^{-3}\ {}^\circ\mathrm{C}^{-1}$) fits the extrapolation of the present data (Fig. 3) whereas the value derived from the later work ($1.61 \times 10^{-3}\ {}^\circ\mathrm{C}^{-1}$) is much lower.

The density behavior of the mercury–indium alloys is typical of nearly all amalgams. The electrical resistivity of most amalgams falls markedly on alloying,[2] notable exceptions being alloys with sodium and potassium. The Hall coefficients of the alloys of mercury with indium[1] and with several other metals[4] show apparent increases in the number of current carriers above those expected on a basis of the solute valency, and these effects have been attributed to the behavior of mercury rather than the solute metal.

X-ray diffraction studies on various mercury–indium liquid alloys[13] show no firm evidence of ordering or structure in the system. The thermodynamics also show small heats of mixing[7] which are not easily reconciled with the large energy which should be associated with the volume contraction.

The effect of adding indium to mercury on the value of various physical properties is shown in Fig. 4. Here the "excess" values of several properties have been plotted as a function of composition with the values normalized at a composition of 30 at. % indium. For this purpose the excess value A_x^{xs} of any property A is defined at composition x as

$$A_x^{xs} = A_x - \{A_1(x) + A_2(1-x)\}$$

where

A_x is the value for the alloy.
A_1 is the value for pure component 1.
A_2 is the value for pure component 2.
x is the atom fraction of component 1.

The number of current carriers per atom (n) in an alloy may be derived from the Hall coefficient (R_H) if the latter is assumed to be correctly given by the free electron expression. The excess value of this parameter (n) has been plotted in Fig. 4 rather than that of the Hall coefficient (R_H). The similarity between the composition dependence of these excess functions is quite striking but at this stage only a very tentative explana-

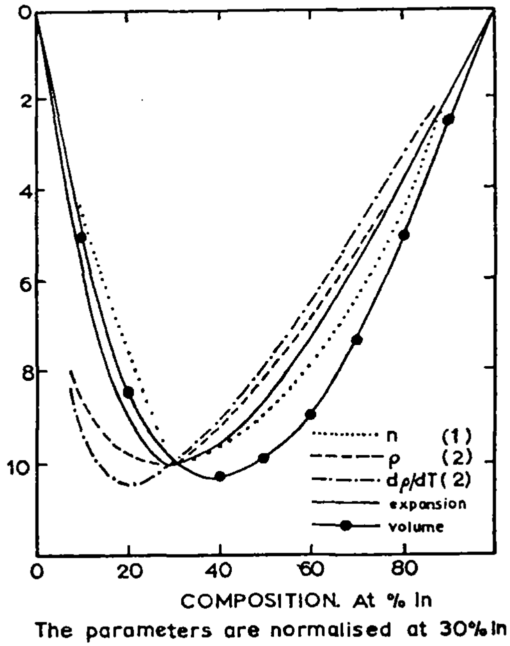

Fig. 4. Excess values for some of the physical properties of the Hg–In system.

tion can be offered. The similar behavior of several mercury systems, and some of the properties of mercury itself, e.g. its high compressibility and expansion coefficient—suggest that the effects are peculiar to the mercury atoms and are relatively insensitive to the second component. It is, suggested that there is a change in the electronic structure of the mercury ion, which accompanies alloying—leading to a more compact ion, and thus an increase in the density. Such an electronic change could absorb energy and account for the small heat of mixing.

At the same time such electronic changes might explain some of the electron transport peculiarities of these systems. The increase in density probably has a small effect on its own, via a change in the thermal vibration spectrum, leading to a difference in the scattering, but Hall coefficient and optical measurements indicate changes in electronic properties which are interpreted in terms of changes in the numbers of current carriers—though at present these parameters are difficult to treat rigorously in a theoretical way.

The possibility that mercury ionizes to give a third electron to the conduction processes, would in principle, fit with the present suggestions. However, considerable further work will be required before such a hypothesis can be substantiated.

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