Viscosity of hg-in amalgam

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1   INTRODUCTION

It seems well established[1] that the viscosity of liquid, in particular a liquid metal, is determined primarily by the strength of interatomic bond and the packing efficiency of the atoms; therefore in a binary system the composition-dependence should provide a sensitive qualitative guide to the manner in which the mean interatomic bond strength varies with composition.

Among the various binary systems the compounds containing systems are very interesting. One of them is the Hg–In (group IIIb) system that presents both from the experimental and from the theoretical point of view some very attractive features:

(a) the system is in its liquid phase at room temperature up to 70% atomic of Indium;

(b) the phase diagram (Figure 1), rather well known[2], shows in the solid phase intermetallic compounds and true non electronic compounds, with various eutectics;

(c) the density versus composition in well known and similarly it is the enthalpy of mixing.[2,3]

For the above reasons we have performed some accurate measurements on the viscosity of Mercury-Indium alloys, both as a function of composition and temperature. In Section 2 of present paper the experimental apparatus is described, together with all the various experimental details and the way in which the rough experimental data have been analyzed. In Section 3 the experimental results are given and in Section 4 their main features and their peculiar characteristics are discussed and some preliminary conclusions are drawn.

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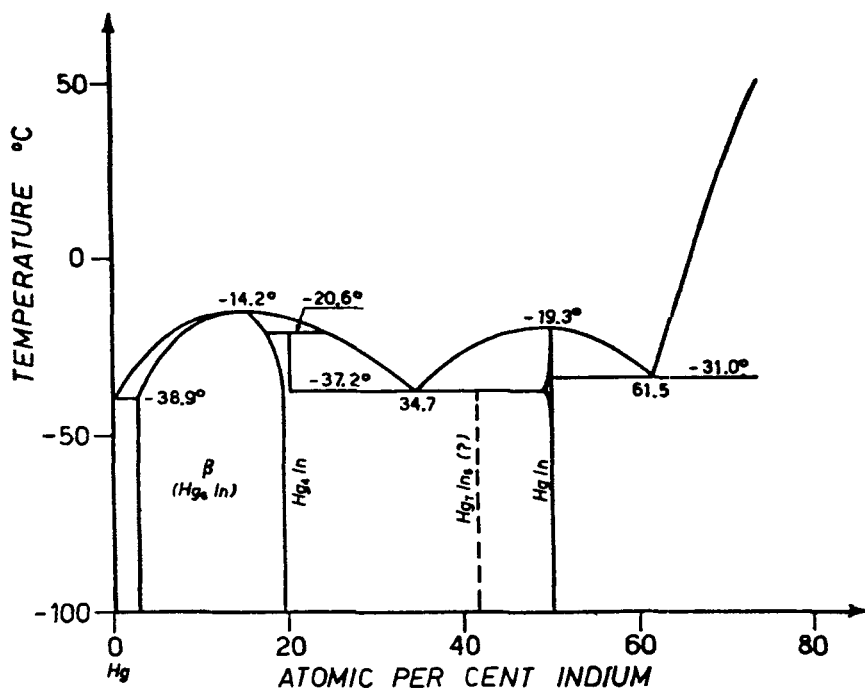
FIGURE 1   Part of the phase diagram of the Hg–In amalgama.

2   EXPERIMENTAL APPARATUS

The viscosity η of Hg–In alloys has been measured using an oscillating toroidal crucible viscometer, whose main features and the complete theory have been fully described elsewhere.[4–5] The liquid sample (≈ 6 cm^3) is contained in a toroidal channel (Figure 2; inner radius a, torus radius R) for which the theory is able to relate the observed damping coefficient δ to the viscosity η of the liquid. Actually from the theory we get that

$$\frac{I\sqrt{2}}{4\Pi^3 A^2 R^3 \rho}\left[\left(1 + \frac{T^2}{T_0^2}\right)\delta - 2\frac{T}{T_0}\delta_0\right] = G_1(q) - \delta\, G_2(q) + \frac{A^2}{R^2}\, G_3(q) \quad (1)$$

where I is the moment of inertia of the empty oscillating system: (T, T_0; δ, δ_0) are the periods and the logarithmic decrements with and without liquid respectively; G_1, G_2, G_3 are universal function of $q = a(2\pi\rho/\eta T)^{1/2}$, tabulated in Ref. (4), and ρ is the liquid density.

By measuring I, T, T_0, δ, δ_0 and knowing separately ρ one solves (1) for q. Once q is determined its very definition allows to get the corresponding value

of η. The above type of viscometer had been chosen in the present experiment for the following reasons:

(a) it has excellent sensitivity and good absolute precision;

(b) the liquid sample, of reduced weight, may be very easily secluded from the oxidising action of the atmosphere.

Actually great care has been used to prepare the liquid samples.

Once In and Hg are weighted to get the desired alloy composition, they are put in two distinct containers connected, together with the viscometer, to a common vacuum line: as soon as a good vacuum ($p \approx 10^{-3}$ torr) is reached everywhere in the vacuum system, In and Hg are brought in contact, and the liquid alloy stirred to get homogeneity. Successively the liquid, opening a valve, is allowed to fill the viscometer. Afterwards the viscometer is disconnected from the vacuum system and few drops of dense silicon oil are quickly poured into the central channel (Figure 2), to protect the amalgama from oxidation during the rapid transfer of the viscometer from the filling bench into a stainless steel vacuum bell. Here the viscometer, suspended through a NiCr thin wire from the bell top, can freely oscillate while it is contained inside an electric furnace, that allows to perform the viscosity measurements at different temperatures.

As soon as all the above preliminary operations are completed, the vacuum bell is evacuated to a very good vacuum ($p \leq 10^{-5}$ torr); successively very pure argon gas is introduced into the bell until a pressure of ≈ 300 torr is reached. The argon atmosphere is important for two reasons:

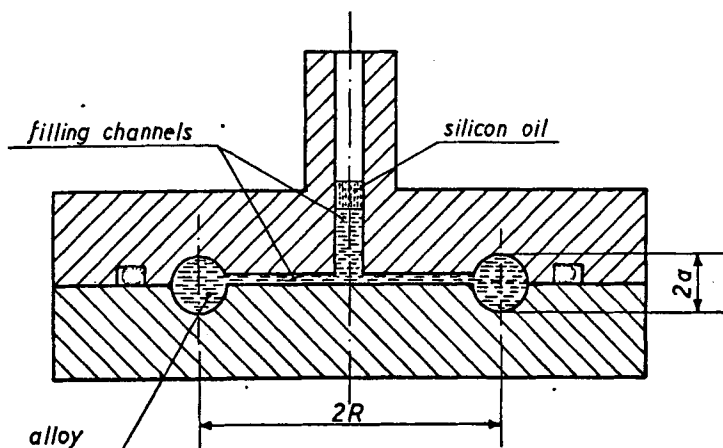(a) a better thermal contact is established between the crucible and the

FIGURE 2   Schematic drawing of the toroidal viscometer.

furnace, that otherwise could be too small to allow the reaching of thermal equilibrium in a reasonable time at the temperatures used in present experiment;

(b) the argon pressure, in spite of the capillary action very important in liquid metals, forces the alloy to return inside the toroidal channel, after it has flown out at high temperature.

One of the most difficult experimental problem was to measure, with sufficient accuracy, the crucible temperature: as a matter of fact any permanent contact with the crucible has to be avoided to allow the viscometer to oscillate freely. We have solved the problem placing inside the furnace two cromel-allumel thermocouple. One of them is fixed and is used to follow the temperature inside the furnace, while, the other is placed directly below the crucible and, by means of a stainless steel rod actuated from outside the bell, is brought in contact with the crucible before and after each damping measurement. The signals from both thermocouples are plotted on a two pen recorder, and contemporary a precision millivoltmeter is employed to measure the signal from the movable thermocouple.

In this way the crucible temperature can be established with an accuracy of $\approx 1°C$. The crucible oscillations were recorded by a Photodyne graphispot: it turned out that the recordings were generally so good to allow the determination of the damping coefficient δ with an accuracy of $\approx 0.2\%$. Both the entire vacuum bell and the graphispot are mounted on oscillation free supports.

3   EXPERIMENTAL RESULTS

The crucible dampings have been measured for each alloy composition (3, 14, 35, 40, 45 atomic percent) at ten different temperatures (from room temperature to $\approx 130°C$). The damping data have been introduced in relation (1) which has been solved using a 135 H.P. calculator. In order to get the absolute values of the alloy viscosities one needs, besides the damping data, the values, at each composition and temperature, of the density. The density values have been obtained from Ref. (3) (see Table I): they have been conveniently interpolated and adjusted to each temperature: for this last purpose use has been made of the expansion coefficient of pure mercury. Actually the uncertainties in the viscosity values due to the bad knowledge of the thermal expansion coefficients are much lower than the ones resulting from the dampings and temperatures data.

The analysed experimental results are plotted in Figure 3 and in Figure 4.

The first figure shows the viscosity as a function of temperature for each amalgama composition, while the second figure shows the viscosity as a

TABLE I

Mole fraction in Mercury	1	0.9	0.7	0.5	0.3	0.0
ρ	13.54(23)	12.76(24)	11.68(24)	10.28(24)	9.01(140)	7.03(175)

The number in parenthesis is the temperature in °C at which the density ρ has been measured.
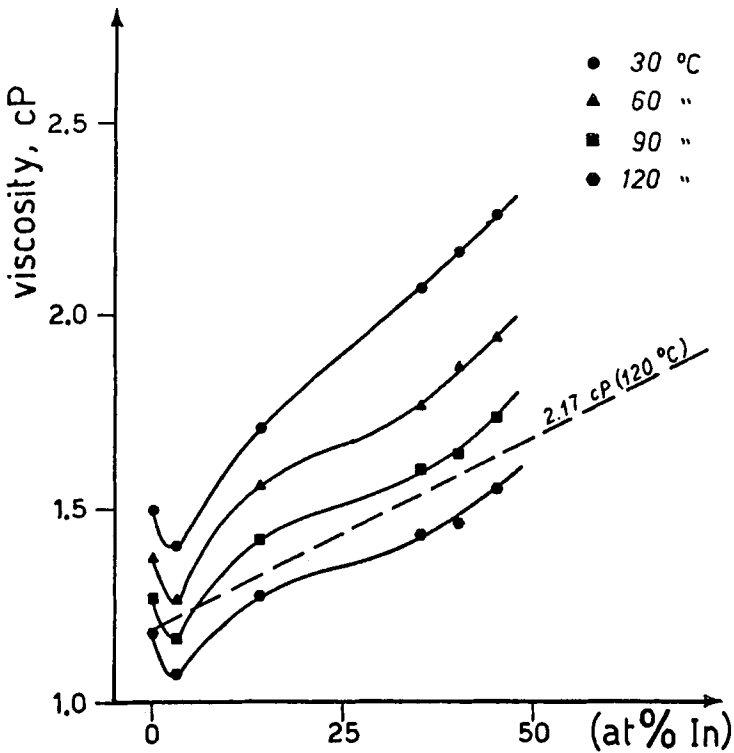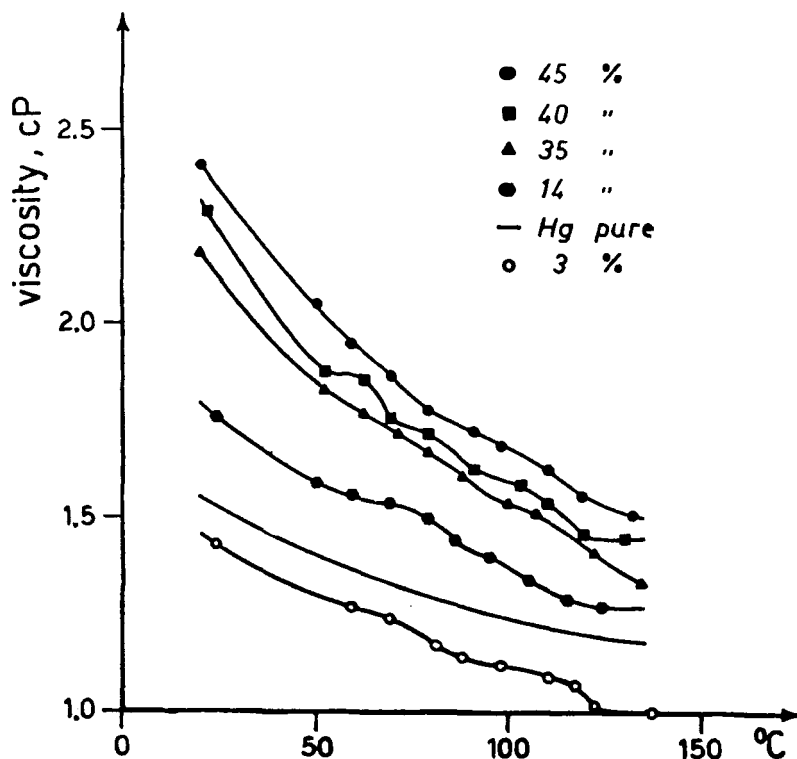
FIGURE 3   Viscosity η versus amalgama composition.

function of the Indium atomic percent at four temperatures (30°, 60°, 90°, 120° C). The pure mercury behaviour, shown in Figure 4, has been taken from the literature:[6] however a few points have been remeasured to check the accuracy of our experimental apparatus.

FIGURE 4   Viscosity η versus temperature.

4   DISCUSSION

The experimental results, collected in Figures 3 and 4, show some interesting aspects.

(a) There is a viscosity minimum at all temperature, for an alloy composition in the neighborhood of 3 at. percent Indium.

(b) There is a gradual increase of viscosity rising the Indium content: however ondulations are superimposed on a linear behaviour obeying the law, valid for a simple two component mixture[7]

$$\eta = \eta_{Hg}\, q_{Hg} + \eta_{In}\, q_{In} \tag{2}$$

where $\eta_{Hy}(\eta_{In})$ is the viscosity of Mercury (Indium) at the same temperature and $q_{Hg}(q_{In})$ is the Hg (In) atomic fraction. The pure Indium viscosity, 2.17 cP at 120° C, has been obtained extrapolating the Arrhenius type law[8]

$$\eta = C \exp (E_\eta / RT) \tag{3}$$

from 206° C, where the Indium viscosity is 1.65 cP, down to 120° C, where pure Indium is already solid. From the literature[9] we know the In "activation energy" E_η to be ≈ 1.2 kcal/mol.

(c) The diagrams of Figure 4 show smooth oscillations, particularly marked around 14 and 40 at. percent In.

Point (a) may be easely explained accepting the old "hole" theory of liquid viscosity. Actually small amounts of In atoms could fill some "holes" of the mercury matrix, lowering therefore the transfer probability of Hg atoms from the actual positions to empty "holes". Being the viscosity, in the holes theory, proportional to the above probability, it seems plausible that the partial filling of "holes" by In atoms could lower the viscosity below the pure mercury value.

Point (b) may be also understood taking into account that the solution of Indium in mercury is far from ideal: in fact all its intermetallic compounds, and in particular the 50 at. percent In, are strongly bound.

Now, according to what has been pointed out in the introduction, greater are the interatomic bonds, greater the viscosity is. At 14, 50 at. percent compositions there is formation in the solid phase of strongly bound interatomic compounds, whose existence could be noticed even in the liquid phase through the residual short range correlations.

The fact that the pure mixture straight line lies always above the experimental points is not clear: one has to take into account, however, the existence of the viscosity minimum around 3 at. percent. Shifting in fact the pure mixture line below the minimum and referring the viscosity to this new line one gets a maximum around 15% and, possibly, another maximum around 50%. Unfortunately, for technical difficulties found in the sample preparation, and in the filling of the viscometer, we could not extend our measurements above 45 at. percent Indium.

(c) By far more difficult is the explanation of the wavy behaviour of Figure 4 diagrams, without a theory of binary alloys viscosity.

To get, however, a deeper insight into this problem we have reconsidered the results of Figure 4, mapping $\ln \eta$ (η in cP) versus $1/RT$ (mol/kcal). If the Arrhenius type law (3) were be strictly valid such diagrams would be straight lines, whose angular coefficient yields immediately the "activation energy" E_η. This phenomenological parameter can, however, be calculated even if the above law is only approximately valid. To this purpose we have used the least squares method,† and the results are reported in Table II and in Figure 5.

In the second row of the table the best values of E_η, ordered according to

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†The numerical calculations have been performed using a HP-25 pocket calculator.

TABLE II

Amalgama composition	0%	3%	14%	35%	40%	45%	100%
E_η (Kcal/mol)	0.61	0.77	0.775	0.98	0.985	0.965	1.2
$1 - r^2$	≈ 0	0.013	0.030	0.09	0.011	0.003	?

the amalgama compositions (at % In), are given, while the coefficient of determination.

$$r^2 = \frac{\left[\sum (\ln \eta_i)/RT_i - \frac{1}{n}\left(\sum \ln \eta_i \sum \frac{1}{RT_i}\right)\right]^2}{\left[\sum (\ln \eta_i)^2 - \frac{(\sum \ln \eta_i)^2}{n}\right]\left[\sum \left(\frac{1}{RT_i}\right)^2 - \frac{\left(\sum \frac{1}{RT_i}\right)^2}{n}\right]}.$$

are listed in the third row. As it is well known,[10] r^2, which spans between 0 and 1, is a measure of the goodness of the linear regression: more r^2 tends to 1, more the experimental points approach a straight line. The above data are also plotted in Figure 5. Finally in Figure 6 the deviations $\ln (\bar{\eta}/\eta)$ from the Arrhenius law are plotted: $\bar{\eta}$ represents the best fit values and η the actual experimental values. By careful examination of Figures 5 and 6 one gets the following temptative conclusions.

(1) Being E_η greater for 3 at. percent than for pure Hg, forcibly C of relation (3) should be much lower in the former case, this conclusion being in agreement with our formerly given temptative interpretation of the minimum: C in fact is proportional to the density of empty "holes".

(2) Both from the indetermination coefficient $(1 - r^2)$ and from the deviations from the Arrhenius law one can conclude that the amalgama composition strongly influences the temperature dependence of η. There are oscillations that seem particularly marked around the compositions corresponding to the formation of intermetallic compounds (14%, 40%). In particular if this last statement is correct, the 40 at. percent composition diagram would strenghten the not yet well established existence of the intermetallic compound $Hg_7 In_5$ (see Figure 1).

In conclusion from the measurements referred in the present paper viscosity seems to be very sensitive to residual short range correlations
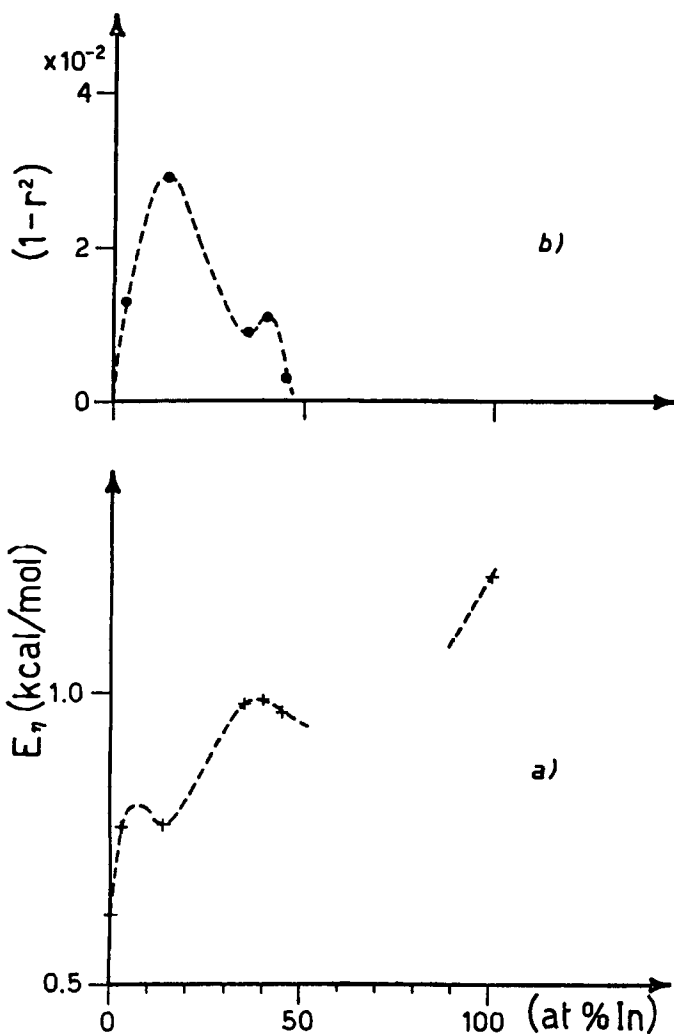
FIGURE 5   Plotting as a function of the amalgama composition:
   (a) of the "activation energy" E_η;
   (b) of the indetermination parameter $(1 - r^2)$.

between atoms in the liquid state, that seem to conserve a memory of the short range correlations found in the solid phase.

Unfortunately a quantitative theory of viscosity, that would allow to interpret the experimental data in term of microscopic parameters, is still lacking, in particular, for binary alloys.
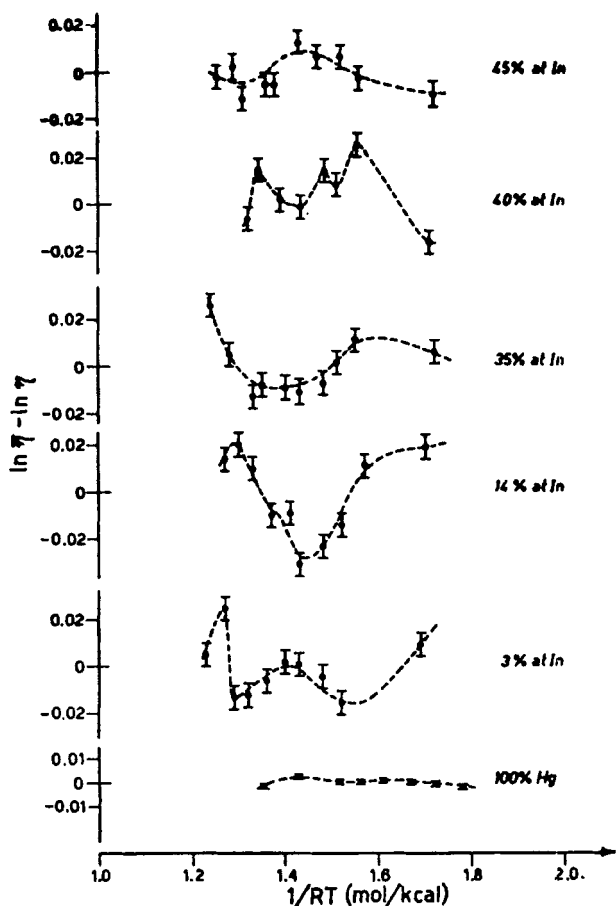
FIGURE 6 Deviations ln $(\bar{\eta}/\eta)$ of the experimental viscosity from the exponential law versus 1/RT for each amalgama composition.

Acknowledgements

SUMMARY

Using a new type of oscillating viscometer, accurate measurements on the Hg–In amalgama viscosity have been performed, at various temperatures, ranging from 20°C to 130°C and for different amalgama compositions

(3, 14, 35, 40, 45 at. percent In). It has been found that the viscosity shows a minimum for small concentration of In; it increases rising the In content, and becomes smaller increasing temperature, deviating however more or less, from the exponential law

$$\eta = C \exp (E_\eta/RT)$$

Taking into account the alloy chemical physical properties, the experimental results are discussed, and some preliminary conclusions about the influence of the residual short range correlations on viscosity are given.

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