

The effect of the addition of antimony on the physical and magnetic properties of iron particles in mercury

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Abstract. Measurements of the resistivity and latent heat of iron-in-mercury magnetic liquids, to which antimony in the form of an antimony-lead eutectic has been added, confirm that the antimony forms a layer about the iron particles. The presence of a monolayer results in a marked reduction of the growth of the particles by diffusion or Ostwald ripening. The addition of antimony to the liquid at 15°C, in quantities greater than that necessary to form a monolayer, results in a reduction in the saturation magnetisation, the magnitude of which depends on the quantity of antimony added.

Iron-in-mercury liquids are highly viscous when more than 1 wt% of iron is present. The addition of antimony to the liquid leads to a much reduced viscosity which permits higher concentrations (about 2.4 wt%) of iron to be dispersed. Magnetic liquids with a saturation magnetisation of 900 G have been prepared using this technique.

1. Introduction

Much work has gone into the study of fine magnetic particles in mercury, reviews of which have been published (Charles and Popplewell 1978, 1980).

Magnetic measurements of iron-in-mercury magnetic liquids show superparamagnetic behaviour. However, in the solid state, i.e. at low temperatures, the magnetic 'liquids' have a coercivity and remanence.

Chantrell *et al* (1978) have shown that the particle size distribution can be obtained from the room temperature magnetisation curves of such systems. Also Luborsky (1962a) has published data which enables the median particle size of iron and cobalt to be determined from a knowledge of their coercivity at 77 K.

There are three important factors which determine the stability of iron-in-mercury magnetic liquids. They are magnetostatic and van der Waals' forces, which lead to aggregation and sedimentation in a gravitational field, and diffusional growth, Ostwald ripening, which leads to particle growth and sedimentation.

Magnetostatic interactions may be rendered insignificant if the magnetostatic energy between adjacent particles is made less than the thermal energy. This can be achieved by reducing the size of the particles present in the liquid. The magnetostatic interaction is less than the thermal energy for iron particles of less than 30 Å.

Van der Waals' forces may be overcome in systems in which the carrier is a non-metal by the use of surfactants which adsorb on the particles and result in an

entropic repulsion between particles. However, no equivalent system has yet been found suitable for liquid-metal carriers (Popplewell *et al* 1976).

Falk and Luborsky (1965) have shown that the addition of metals to iron-in-mercury magnetic liquids inhibit diffusional growth at high temperatures. The most effective of these additives are tin and antimony. Luborsky (1962b) postulated that the additive formed monolayer coatings on the particles, the area covered per atom of adsorbate being $A = \sqrt{3}(M/2\rho_{\text{ad}}N)^{2/3} \text{ cm}^2 \text{ atom}^{-1}$, where M is the atomic weight, ρ_{ad} is the density of the additive and N is Avogadro's number. In this paper the effect of the addition of antimony on the diffusional growth at high temperatures is discussed.

A homogeneous distribution of iron particles in mercury will, when left undisturbed in a gravitational field, achieve equilibrium. The equilibrium concentration profile will depend on the difference in densities of the particles and mercury and on the particle size distribution. The rate at which equilibrium is achieved will give information concerning the size of the particles or aggregates of particles, if present. A study of the approach to equilibrium has been made on iron particles in mercury, with and without additives, the results of which are presented in this paper.

Iron-in-mercury magnetic liquids become highly viscous when the iron concentration exceeds 1 wt% (Hoon *et al* 1979), and thus the maximum value of the saturation magnetisation of the liquid is severely limited. The results of an investigation of the effect of the addition of antimony on the viscosity of these liquids is included in this paper.

Hoon *et al* (1978) have shown that measurements of the resistivity and of the latent heat of fusion of these liquids with and without additives enable information concerning the distribution of the additives in the liquids to be obtained. The results of similar investigations with antimony as the additive are presented.

2. Experimental procedure

Fine iron particles of approximately 30–40 Å median diameter were prepared by electrodeposition of iron from a 280 g per litre ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) electrolyte into a vibrationally and magnetically agitated mercury cathode.

Because of the very low solubility of antimony in mercury (2.9×10^{-5} wt% at 18°C, Tamman and Hinuber 1927) the addition of antimony was achieved by dissolving an antimony-lead eutectic alloy (11.1:88.9 wt%) in the iron-in-mercury magnetic liquid. This alloy, known as 'magnolia' alloy, was produced by melting antimony and lead *in vacuo* at 800°C.

Magnetic measurements on the liquids were made at room temperature and at 77 K (in the solid state) using a vibrating sample magnetometer.

The electrical resistivity of the liquids was measured at room temperature using a standard four-probe method with current reversal.

An investigation of the solid-liquid transition of the magnetic liquids was carried out using a differential scanning calorimeter (Perkin-Elmer DSC 1).

The concentration profile of the iron particles in the magnetic liquid contained in a vertical column was measured as a function of time. The concentration profile was monitored by measuring the change of inductance of a coil measured by a Wayne-Kerr autobalance universal bridge (type B641) as the column of liquid was lowered through the coil.

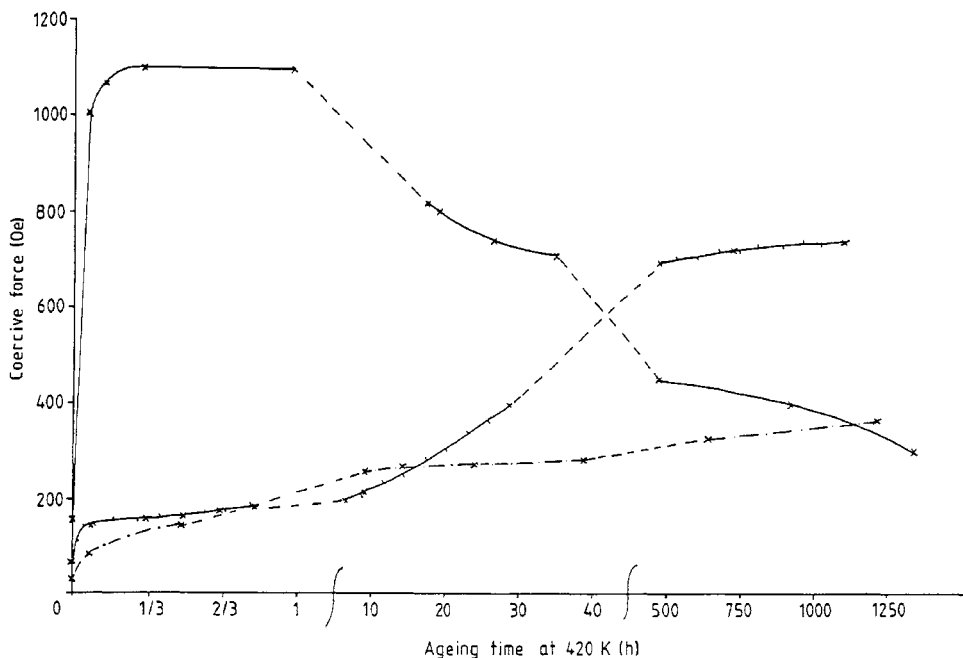


Figure 1. Effect of coatings on coercivity ageing curves at 420 K. —, no coating; - - -, 0.44 g Sn/g Fe tin coating; — · — · —, 0.14 g Sb/g Fe antimony coating.

A Poiseuille flow viscometer was used to measure the viscosity of the magnetic liquids.

Analyses for iron and antimony were made using an atomic absorption spectrophotometer (Pye-Unicam SP 2900).

3. Results and discussion

3.1. Magnetic measurements

Iron-in-mercury magnetic liquids are superparamagnetic in the liquid state. However, in the solid state, they possess a coercivity and remanence. Antimony-lead alloy (11.1 wt% Sb:88.9 wt% Pb) was added to a 0.511 wt% iron-in-mercury liquid with an initial particle diameter of 28 Å. The alloy was added in sufficient quantity to form a monolayer of antimony on the particles. The quantity required was based upon the equation derived by Luborsky (1962b) modified to take into account the particle size distribution (Chantrell 1977).

Figure 1 shows the variation of the coercivity H_c at 77 K with time, for liquids aged at 420 K. Three liquids were studied; an untreated iron-in-mercury liquid and two samples with tin and antimony added in sufficient quantity to form a monolayer about the particles. All three samples were taken from the same preparation to ensure that the particle size distributions were as similar as possible. The untreated sample and the one with tin added were used as controls. It can be seen from figure 1 that the coercivity of the liquid containing the untreated particles grew rapidly and achieved a

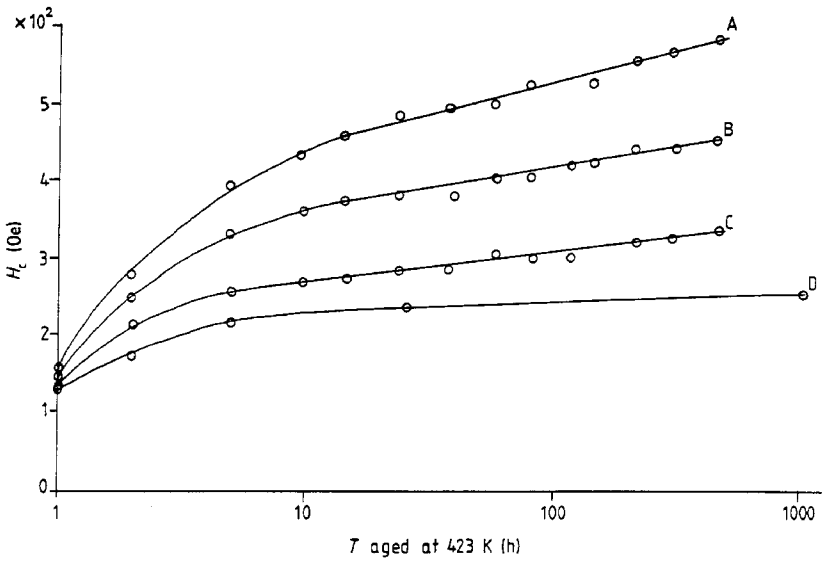


Figure 2. The stabilisation effect on particles due to antimony coatings. Values (in g Sb/g Fe) for curve A = 0.08, for curve B = 0.1, for curve C = 0.145 and for curve D = 0.31.

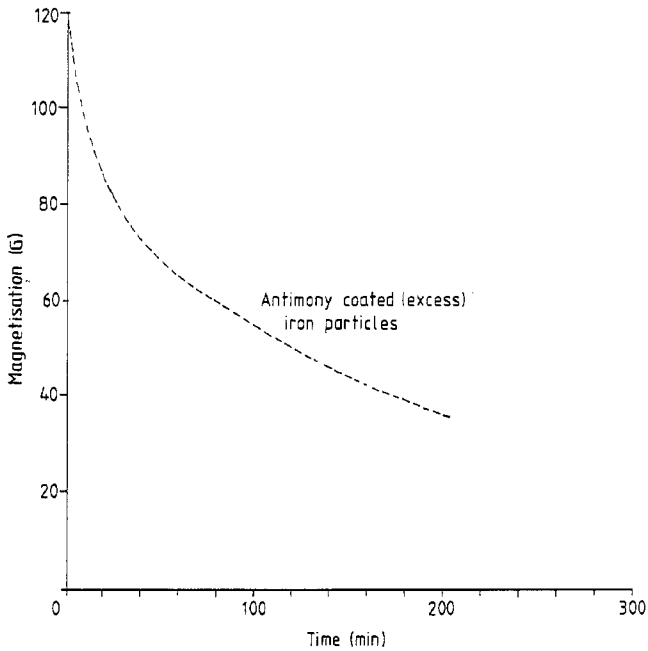


Figure 3. Reduction of the saturation magnetisation for an iron-in-mercury liquid containing excess antimony at 420 K.

maximum in the first 20 minutes of ageing. In comparison, the sample containing tin showed a much slower growth in coercivity. These results are consistent with those of Windle *et al* (1975) and indicate that particle growth is occurring. The sample containing antimony showed a much reduced increase in coercivity indicating that antimony is much more effective in inhibiting diffusional growth at 420 K than tin.

Figure 2 illustrates the effect on the growth of iron particles in mercury at 420 K of the addition of different quantities of antimony alloy. The samples of iron particles in mercury used were taken from the same preparation containing 0.5 wt% Fe with a particle diameter of 30 Å. 0.31 g Sb/g Fe corresponds to a monolayer of Sb on a log normal distribution of particles of median diameter 56 Å and standard deviation $\sigma = 0.65$ (Kneller and Luborsky 1963). Very little change in coercivity with time occurred after ten hours ageing at 420 K. This can be attributed to the cessation of growth. The value of the coercivity corresponds to a median diameter of 50 Å according to Luborsky (1962a). This value corresponds very closely with the value given above, calculated assuming a monolayer coating of Sb. The other curves correspond to the addition of smaller quantities of Sb. In these cases, growth, i.e. an increase in coercivity with time, could be expected to continue until the quantity of antimony present corresponds to a monolayer. For example, 0.08 g Sb/g Fe would be sufficient to form a monolayer coating on a particle distribution with median diameter 180 Å corresponding to a coercivity of about 10^3 Oe.

The results shown in figure 3 indicate that if antimony is added in excess of the concentration to form a monolayer, then the excess reacts with the iron particles on thermal ageing with the result that the saturation magnetisation is reduced.

3.2. Resistivity measurements

The effect of the addition of lead and of the Sb–Pb alloy on the resistivity of a 0.58 wt% iron-in-mercury liquid and of pure mercury is shown in figure 4.

Curve A shows that the electrical resistivity of pure lead in mercury at room temperature falls almost linearly with increasing lead concentration until 1.2 wt% lead at which the resistivity rises sharply. This concentration corresponds to the solubility limit of lead in mercury at room temperature. A similar effect was observed by Hoon *et al* (1978) for the addition of tin to mercury.

Curve B shows the resistivity of the iron-in-mercury liquid as a function of lead concentration. Again, the curve turns up at 1.2 wt% lead. Hence it may be inferred that the lead remains in solution and is not deposited on the particles to form a coating.

Curve C shows the resistivity of the Sb–Pb alloy in mercury as a function of the lead concentration present. The resistivity curve is higher than any of the other curves and may be due to the presence of fine undissolved antimony particles in the liquid since it appears from the position of the up-turn in the curve that the lead is in solution. It is known (Tamman and Hinnuber 1927) that for concentrations of antimony in excess of that required to form the eutectic alloy with lead that the excess exists as small particles of pure antimony and not as an intermetallic with lead.

The fact that curve D, which shows the resistivity of the iron-in-mercury liquid containing the Sb–Pb alloy as a function of lead concentration, exhibits a similar behaviour to curve B and is quite different from curve C would seem to confirm the results of Falk and Luborsky (1965) and indicate that antimony is not present as fine undissolved particles but associated with the Fe particles as a coating.

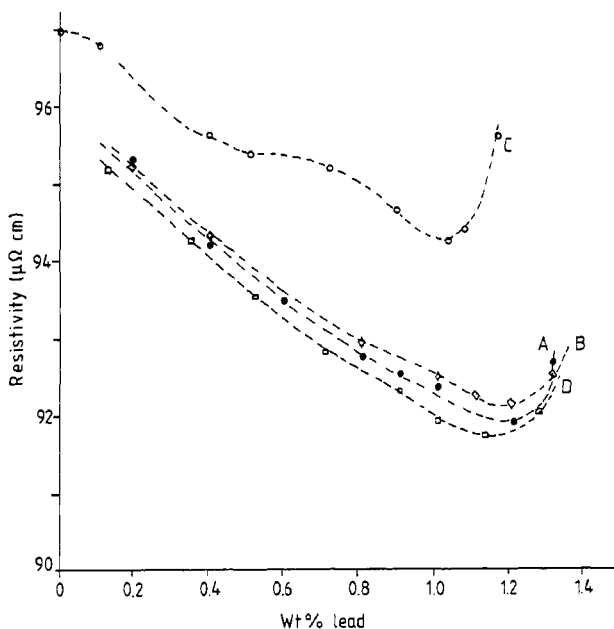


Figure 4. The variation in the resistivity of antimony-lead additive liquids. ● Hg-Pb; ○ Hg-Pb-Sb; ◇ (0.58 wt% Fe) + Hg-Pb; □ (0.58 wt% Fe) + Hg-Pb-Sb.

3.3. Differential scanning calorimetry

Figure 5 shows the line shape produced by the differential scanning calorimeter when scanning from low to high temperatures through the melting point of various samples. The area under the curves is a measure of the latent heat of fusion. Isothermal lines are inclined to the line shape base line defined by the leading edge of the melting transition. For the samples, other than pure Hg, significant premelting occurs, indicated by the symbol Q_p . Premelting is normally a measure of the impurity of a system.

In figure 6, the area under the curve defined by Q_p normalised with respect to the total heat of transition is plotted as a function of the iron content of the system. The addition of Pb to the Fe-Hg system produces a significant change in the plot. The addition of the same quantity of Pb, but in the form of the Sb-Pb alloy produces a plot which is virtually identical with the sample containing Pb additive only. It would therefore appear that the presence of antimony has had little or no effect on the melting transition. This result can be interpreted as indicating that the antimony does not remain in solution but is associated with the iron particles. However, although other explanations are possible, the data do not in any way conflict with the observations of the resistivity measurements.

3.4. Spectrometric analysis

Application of a strong magnetic field gradient to the magnetic liquids enables magnetically strong liquids to be produced and separated from a weakly magnetic mercury residue.

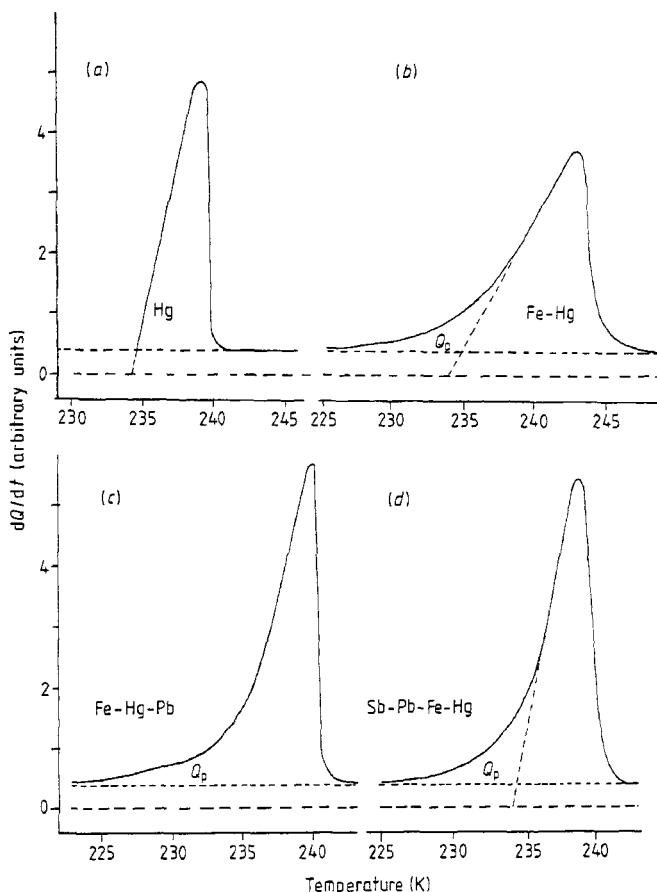


Figure 5. Melting curves for various samples.

A 0.6 wt% iron-in-mercury liquid, containing sufficient antimony to form a monolayer on the iron particles, was subjected to a magnetic field gradient of 10^3 Oe cm^{-1} . The weakly magnetic mercury was poured off.

Spectrometric analysis of the two fractions for iron and antimony showed that 99.5% of the iron and 96.2% of the antimony resided in the magnetically strong fraction. This indicates that the bulk of the antimony is associated with the iron in the magnetically strong fraction and is not in solution. If the latter situation had applied then there would have been an equal concentration of antimony in both fractions.

3.5. Gravitational settling

The approach to the equilibrium concentration distribution of iron particles in a 0.5 wt% iron-in-mercury liquid contained in a 14 cm vertical column has been examined in a gravitational field. Rapid upward settling of the iron particles occurs which is not representative of a distribution of iron particles of median diameter 35 Å. The effective particle size in the column of liquid may be obtained using Stokes law:

$$\frac{4}{3}\pi r^3(\rho_{\text{Hg}} - \rho_{\text{Fe}})g = 6\pi\eta r v$$

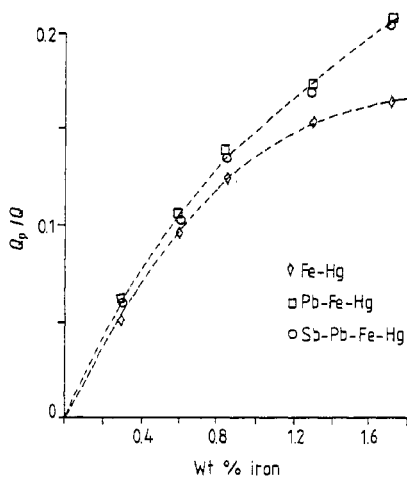


Figure 6. The ratio of the premelting heat to the total heat of transition as a function of the concentration.

where r is the radius of an iron particle, η is the viscosity of mercury and v is the terminal velocity of the particles moving in the mercury. Thus the diameter is given by

$$d^2 = 18\eta v / g(\rho_{\text{Hg}} - \rho_{\text{Fe}}).$$

The velocity of the particles was measured from the movement of the lower edge of the concentration profiles giving an effective diameter of 5.4×10^{-4} cm, far greater than the diameter of an individual particle. This result has been attributed to the fact that the particles in the liquid exist in large agglomerates. Similar results have been obtained by Hoon *et al* (1979) on mercury systems and Peterson *et al* (1974) on magnetite in water.

Results for the antimony-coated system show that the movement of the lower edge of the concentration profile is somewhat slower than that for the uncoated system. It is clear that the presence of antimony has had little effect on the degree of agglomeration.

3.6. Viscosity measurements

The viscosity of iron-in-mercury liquids is much larger than might be expected from theories which assume individually dispersed particles (Kruyt 1952, Rosensweig *et al* 1965). The dramatic change in viscosity with increasing particle concentration as shown in figure 7 is consistent with the occurrence of open-structured aggregates. The presence of aggregates, around 10^4 Å diameter, is consistent with the sedimentation data presented in this paper. Further, the presence of aggregates can account for the thixotropic behaviour of the liquids. The effect of shear-thinning is illustrated in figure 8 for a 2.1 wt% iron sample. The effect of an increase in shear is to reduce the average size of the aggregates, thereby reducing the viscosity. Figure 8 also shows that the addition of antimony, in the form of a Pb alloy, leads to a significant reduction in the viscosity of the system. In fact, the appearance of the material changes from that

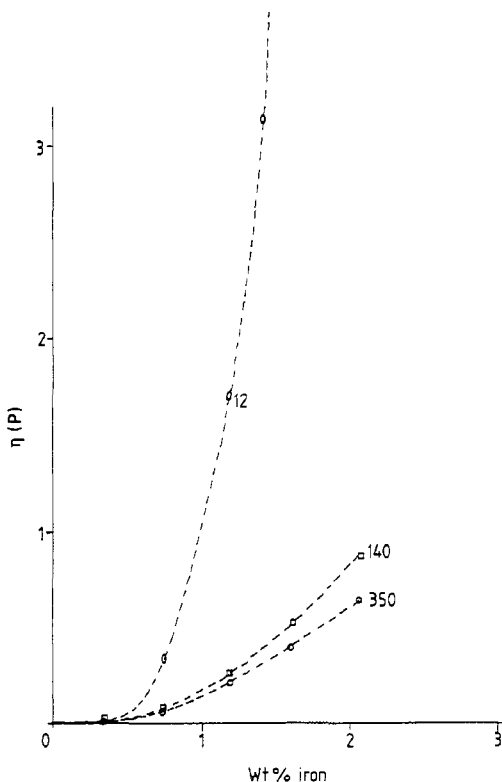


Figure 7. Viscosity of an iron-in-mercury magnetic liquid as a function of iron concentration. Values of the shear rates (in cm^{-1}) are given against each curve.

of a paste to a liquid. A control experiment, in which lead alone was added, did not show a similar reduction of viscosity, indicating that the presence of antimony is essential.

All the evidence presented in this paper indicates that the addition of antimony leads to the formation of a coating of antimony on the particles. The reduction in viscosity on the addition of antimony may arise because the increased separation of the magnetic cores reduces interparticle magnetostatic forces.

The mean iron particle size (approximately 50 \AA) for the data presented here is larger than that (approximately 30 \AA) needed for kT to overcome the magnetostatic forces. The reduction in interparticle forces could either result in a reduction of the size of the open-structured aggregates, although sedimentation data indicates that the reduction is not marked, or simply a loosening of the binding between the particles constituting each aggregate. The role of van der Waals' forces is, however, not clear.

The saturation magnetisation of the as-prepared liquids can be increased by magnetically concentrating them in a strong magnetic field gradient and allowing the non-magnetic mercury to fall from the sample under gravity. The factor which limits this concentration process is the viscosity. The addition of antimony has enabled the magnetic concentration to be increased, so that liquids possessing magnetisations of up to 900 G have been prepared.

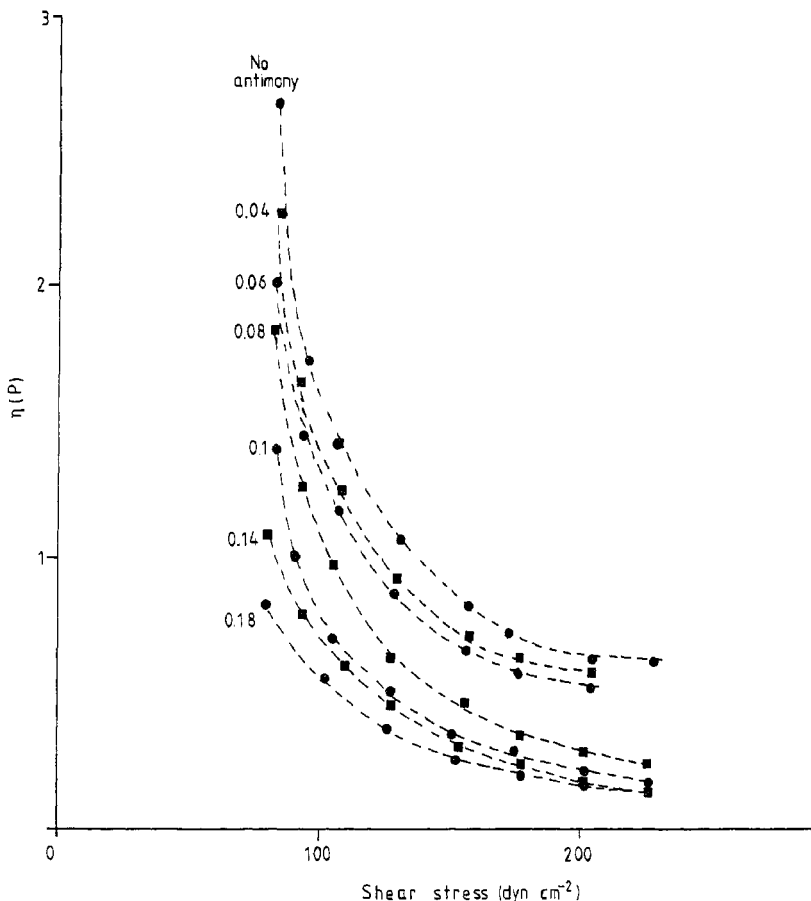


Figure 8. Viscosity versus shear stress for a 2.1 wt% iron-in-mercury fluid with various different concentrations of antimony, given in g Sb/g Fe against each curve.

4. Conclusions

Liquids consisting of iron particles in mercury exhibit superparamagnetic behaviour in the liquid state but become ferromagnetic in the solid state, i.e. they possess a remanence and coercivity. Measurements of the coercivity enable the mean particle size to be determined. When the magnetic liquids are aged at 423 K, the coercivity increases indicating that particle growth by Ostwald ripening is occurring. The addition of antimony in the form of a Sb-Pb eutectic alloy, in sufficient quantity to form a monolayer coating about the iron particles, prevents particle growth. The amount needed to prevent particle growth gives an independent measure of the mean particle diameter. The formation of an antimony coating is confirmed by resistivity, calorimetric, analytical and magnetic measurements. Excess antimony, over and above that required to form a monolayer, results in the reduction of the saturation magnetisation of the liquid. This reduction is consistent with diffusion of antimony into the iron core of the particles. The Pb component of the eutectic remains in solution and is not associated with the iron particles.

Measurements of the sedimentation rates of the iron particles in a gravitational field indicate that the particles exist in aggregates of about 10^4 \AA . This is consistent with the observations of the movement of the magnetic material within the liquid in strong magnetic field gradients. The viscosity and thixotropic behaviour of the liquids is also consistent with the presence of loose-structured aggregates. The reduction in viscosity on the addition of antimony is attributed to the formation of a coating about the particles resulting in an increase in the separation of magnetic cores and a reduction of the magnetostatic forces between the particles.

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