A New Technique for the Preparation of Metallic Magnetic Fluids from Metal Atoms

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A new technique for preparing metallic magnetic fluids by the low temperature decomposition of a toluene–cobalt complex formed from cobalt atoms is reported.

Colloidal suspensions of fine magnetic particles, magnetic fluids or 'ferrofluids,' have a wide range of technical applications.[1] Commercial fluids are limited to ferrite particles prepared by size reduction (grinding) or precipitation techniques. The greater magnetisation of metallic Fe, Co, and Ni and the potential tailoring of magnetic properties such as Curie temperatures by the use of metal alloys, makes the preparation of small metallic particles desirable. Cobalt,[2] iron,[3,4] nickel,[5] and more recently alloy[6,7] particles have been prepared by the thermal or photolytic decomposition of suitable organometallic compounds in hydrocarbon media in the presence of surfactants. In this paper we describe a novel variant of this procedure in which the low temperature decomposition of a toluene–cobalt complex, formed from cobalt atoms, in the presence of a surfactant, yields a ferrofluid with excellent magnetic properties. This method is particularly adaptable to the preparation of alloy systems[8] with wide ranging composition and this represents an important new technique for preparing magnetic fluids. Powders are obtained in the absence of suitable surfactants.[9,10] Recently metal evaporation into a low vapour pressure hydrocarbon oil at ambient temperature, followed by annealing at 270 °C was briefly reported to yield metal particles of small size.[11]

In an experiment lasting 80 min, 7 g (83 mmol) of cobalt vapour was condensed into a solution of 6.78 g (30 mmol) of Manoxol-OT[†] (**1**) in 150 cm^3 of toluene. The solution was contained in the 10 dm^3 glass flask of a modified G.V. Planer rotary solution reactor, and was cooled to −90 °C. As the cobalt condensed, the solution became yellow, then green, then black. When condensation was complete, the rotating flask was allowed to warm to room temperature under an atmosphere of nitrogen. The final black slurry was filtered through powdered quartz to yield a black colloidal suspension (see below) which could be pumped down to a sticky toluene-free mass and redispersed in toluene. About 80% of the original Manoxol and 44% of the condensed cobalt were present in the colloid.

$$\mathrm{NaO_3SCH(CO_2C_8H_{17})CH_2CO_2C_8H_{17}}$$

(**1**)

$$\mathrm{Me[CH_2]_7CH{=}CH[CH_2]_7C({:}O)N(Me)CH_2CO_2H}$$

(**2**)

The resulting colloid was examined using transmission electron microscopy which revealed well dispersed, approximately spherical particles. Micrograph prints of total magnification *ca.* 600 000 were examined using an automated image size analyser to obtain a physical particle size distribution. The particle size distribution was found to be Gaussian with a mean particle diameter of 5.0 nm and standard deviation of 0.6. This compares favourably with the organometallic route which typically leads to values of 7.0 nm and 1.0[6,7] respectively. Narrowness of particle size distribution is an important feature in magnetic fluids and the new technique is most successful in attaining this criterion.

The room temperature magnetisation curve of the colloid in toluene (*ca.* 8.7% w/w Co) was measured using a vibrating sample magnetometer. The fluid was found to be superparamagnetic with a slow rise to saturation consistent with small particle size. The saturation magnetisation of the fluid was found to be 10.5 J T^{-1} kg^{-1}, a value which may be varied by altering the quantity of toluene used during redispersion. This value represents a magnetic mass fraction of approximately 6.3% whilst analysis of the magnetisation reveals a magnetic particle diameter of ~3.0 nm. Both of these quantities are smaller than the corresponding physically determined values which is normally the case for metallic magnetic fluids and is ascribed to a magnetically 'dead' layer on the surface of the particles which may be due to oxidation, surfactant reaction, or spin pinning. The magnetic properties of the new fluid are thus very similar to those prepared *via* the organometallic route with improved particle size distribution and good metal content.

An EXAFS spectrum of the fluid, obtained using a laboratory scale spectrometer, deviated only slightly from that obtained for the bulk material indicating that most of the cobalt is in a metallic environment. The i.r. spectrum of a toluene-free Manoxol–cobalt film was the same as that of pure Manoxol. This and the EXAFS results suggest that only a small fraction of the cobalt is chemically bonded to the Manoxol.

We believe that the primary reaction of cobalt atoms is with the toluene solvent to form an unstable toluene–cobalt complex.[9] This decomposes slowly at −90 °C and more rapidly on warming to room temperature forming cobalt particles. The Manoxol surfactant is presumably chemisorbed on the surface of the particles and may assist in limiting particle growth and achieving a narrow range of particle size.

We have also studied the condensation of cobalt and iron atoms with toluene solutions of Sarkosyl-O[†] (**2**). In this case, the solutions exhibited no strong magnetism until all the Sarkosyl had been converted to a complex of type M(Sarkosyl)$_2$, where M = Co^{II} or Fe^{II}. The i.r. spectrum of these complexes show no ν (C=O) band at 1720 cm^{-1} which is very strong in the free Sarkosyl. With cobalt, after complexation is complete a stable ferrofluid can be formed by further addition of cobalt vapour.

We are exploring the capabilities of this atom approach for forming magnetic fluids composed of mixed-metal 'alloy' particles. The exciting possibility of preparing colloidal rare-earth metals such as gadolinium, with very low Curie temperatures, is also under investigation and may significantly enhance the applicability of magnetic fluids.

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[†] Manoxol is a tradename of Manchem Ltd., and Sarkosyl a tradename of Ciba-Geigy Ltd.