

## SYNTHESIS OF TBP-BASED FERROFLUIDS

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Keywords: magnetic particles, ferrofluids, stabilized colloids, carriers

### **Abstract**

*The synthesis and the systematic study of the properties of magnetic fluids (magnetic dispersions) were started a few years ago. Ferrofluids consist of ca. 100 Å diameter particles of a magnetic solid (usually magnetite, Fe<sub>3</sub>O<sub>4</sub>) colloidally suspended in a carrier fluid. Typical carrier fluids include hydrocarbons, water, fluorocarbons, esters, diesters, organometallics, polyphenyl ethers, and silicones. Surfactants such as oleic acid and other small molecules as well as a few polymers have been used to coat the surface of microcrystalline Fe<sub>3</sub>O<sub>4</sub> to help prevent particle flocculation.*

*In this work, magnetic liquids based on tributylphosphate (TBP) with ferrophase content of 20 to 60 wt% were prepared by precipitation of magnetite from ferric and ferrous salts with the help of an excess of concentrated ammonia or strong base followed by stabilization with the help of 10-undecenoic acid as surfactant.*

### **Introduction**

Finely divided magnetic matter is important in many areas of science and technology. These include ferrofluids, which are colloids of magnetic particles dispersed in carrier fluids[1].

Colloidal solutions of nanoscaled magnetic particles ("Ferrofluids") are stabilized against coagulation either by electrostatic repulsion or by coating the core with organic chain molecules acting as surfactants [2].

In recent years, the development of a variety of methods for producing relatively well-characterized colloidal particles with a narrow size distribution and uniform composition has stimulated experimental work, new theoretical ideas and the development of simple computer models [3].

In this work, magnetic liquids based on tributylphosphate (TBP) with ferrophase content of 20 to 60 wt% were prepared by precipitation of magnetite from ferric and ferrous salts with of an excess of concentrated ammonia or strong base followed by stabilization with the help of 10-undecenoic acid as surfactant.

## Experimental

Authors reference themselves [4], but Source #1 references Bee et al from 1990.

### Preparation of magnetite

Magnetite was precipitated by dissolving  $\text{FeSO}_4$  and  $\text{FeNH}_4(\text{SO}_4)_2$  in demineralized water and adding sodium hydroxide to this solution while stirring vigorously [4]. After sedimenting the precipitate with permanent magnet, the supernatant was removed by decantation. 2 M  $\text{HClO}_4$  was then added to the black sediment and the mixture was stirred for 10 minutes. The oxidation was completed by adding  $\text{Fe}(\text{ClO}_4)_3$  to the mixture and stirring it at its boiling temperature for 2 h. After sedimentation and washing with 2 M  $\text{HClO}_4$ , the reddish yellow sediment,  $S_1$ , contained ca. 10% solid material.  $S_1$  dispersed by adding demineralized water and resulting black dispersion,  $D_1$  was characterized by electron microscopy (TEM).

Reference missing. Source #1 references Bee et al from 1990.

### Grafting magnetite with unsaturated acids

$D_1$  was diluted by adding demineralized water and the sol was flocculated by adding few drops of 25%  $\text{NH}_3$ , and sedimented using a permanent magnet. After washing, four times, with demineralized water new ferrophase was diluted and under mechanical stirring some unsaturated acids or their salts was added. Within a few minutes, all magnetic materials was transferred in chloroform phase. The black chloroform droplets were separated from the colorless water phase and washed few times with aqueous ethanol solutions to remove excess surfactant. After room drying the particles redispersed easily in tributylphosphate for obtaining a new ferrofluid, TBP - FF.

The FTIR spectrum of some dried products give interesting information about bonds between unsaturated acids and magnetic particles.

Thermogravimetry was performed by heating some powders from room temperature to 900 °C at a rate of 10 °C/min.

Authors reference themselves [4], but Source #2 is actually T. Osman et al. from 2001.

## Results and Discussion

Ferrofluids are an interesting group of liquids, because they have liquid properties and act like ferromagnetic materials [4]. Many properties of the ferrofluid are similar to those of the base fluid. Since the concentration of magnetic particles is low, 3-10%, they do not affect the density, vapor pressure, pour point, or chemical properties of the liquid, but there is an increase of the ferrofluid viscosity compared with the viscosity of its base fluid [5].

Applications of ferrofluids are usually based on their controllability by external magnetic force [6].

Same reference as Source #2 this time.

Name of reactants were changed but no quantities are given, unlike the authors of Source #1

Also, [4] is by the same authors and contains the same picture shown here in Fig 2, taken from 1993

See below

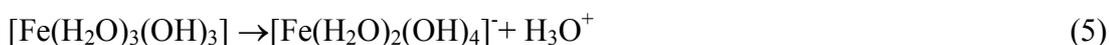
In our case utilization of TBP and unsaturated acids give new possibility of work in separation processes with ferrofluids based solubility of many compound in this solvent and derivative capability of grafted acids.

Modified Massart procedure to obtaining *magnetite nanoparticles* consist in following reaction [7]:



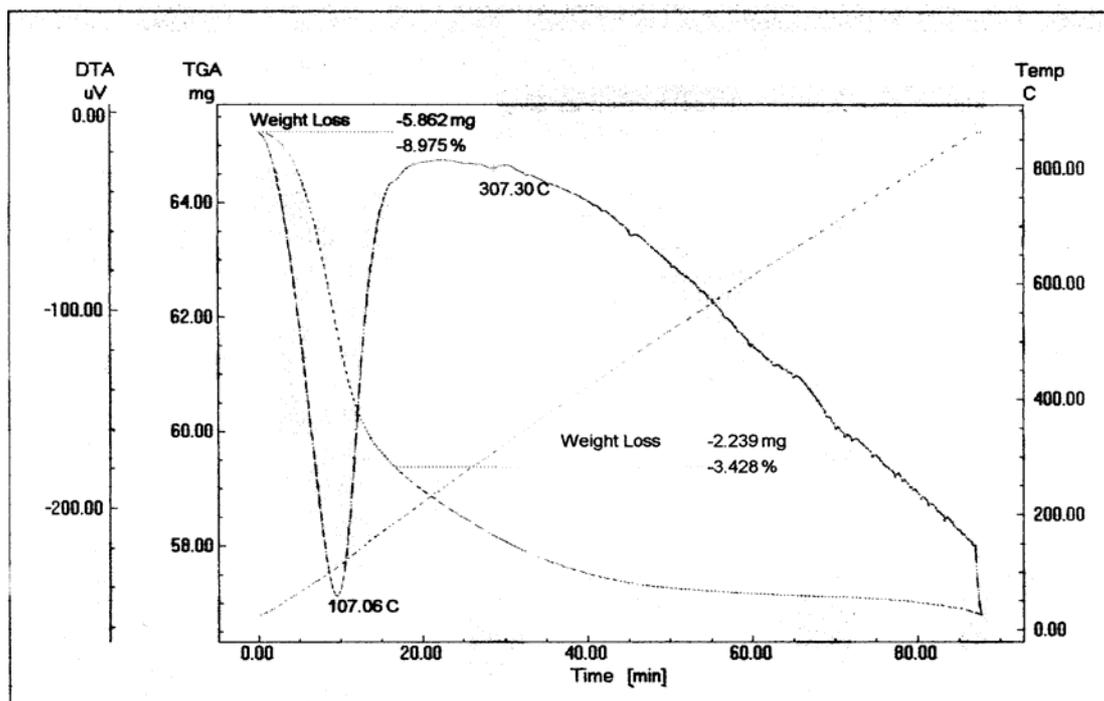
This reaction was justified by cation hydrolysis

For example  $\text{Fe}^{3+}$ , hydrolysis have following steps:



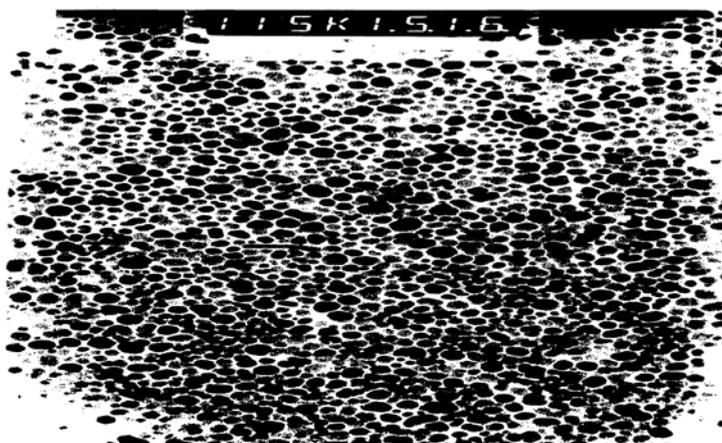
The acidity needs a permanently control of pH by sodium hydroxide concentration, and from this reason ammonia of ferros or ferric salts was used in modified Massart procedure [8].

Magnetite nonoparticles have a oxidic core and hydroxo-complex surface wich is evidenced by thermogravimetry (fig. 1). The magnetite nanoparticles loss all water to 107 °C.



**Figure 1.** Thermogravimetry of magnetite nanoparticles

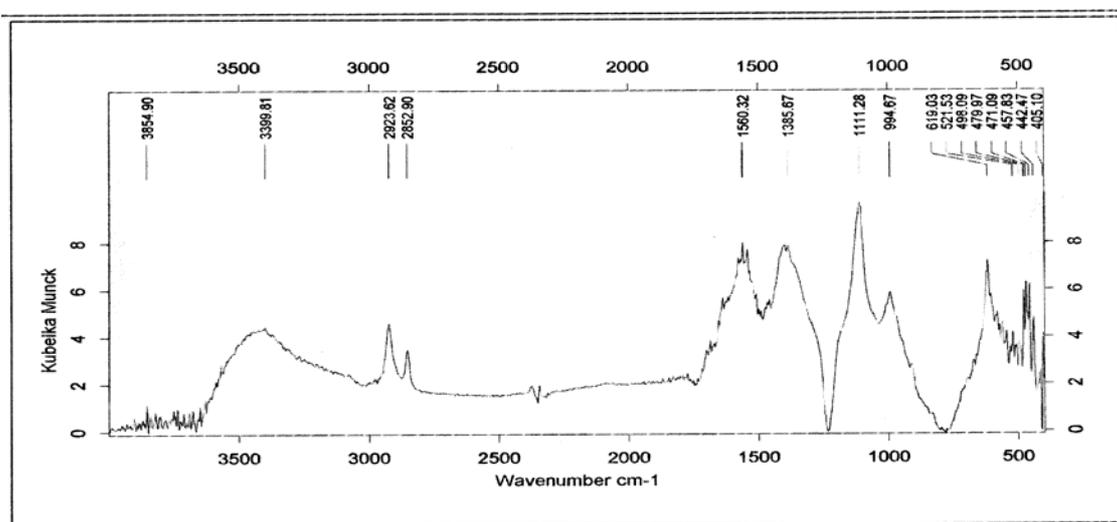
After complete hydrothermal procedure magnetic nanoparticles was transferred in chloroform and after this in TBP with unsaturated acids as stabilizing agent (fig. 2).



Picture taken from paper published in 1993 by different authors (not referenced). See the Head-to-Head comparison.

**Figure 2.** Magnetic nanoparticles 15-20 nm in TBP-ferrofluid

In all cases utilization of unsaturated acids (10-undecenoic or oleic acids) or their salts (ferro-, ferri-, ammonium or sodium oleate) gives a characteristic spectrum (fig. 3).



**Figure 3.** Specific FTIR spectrum of covered magnetic nanoparticles with unsaturated acids (10-undecenoic acid)

The FTIR spectrum of dried products shows peaks of 1385,67 and 1560,32  $\text{cm}^{-1}$  which correspond to the symmetric and asymmetric stretching of carboxylate groups [9]. The presence of carboxylate groups shows that condensation reaction has occurred between the

hydroxylated magnetic surface and unsaturated acids. The strong C=O stretching vibration ( $\sim 1720\text{ cm}^{-1}$  from free 10-undecenoic acid – fig. 4) is absent; apparently washing the precipitate removes all free unsaturated acid.

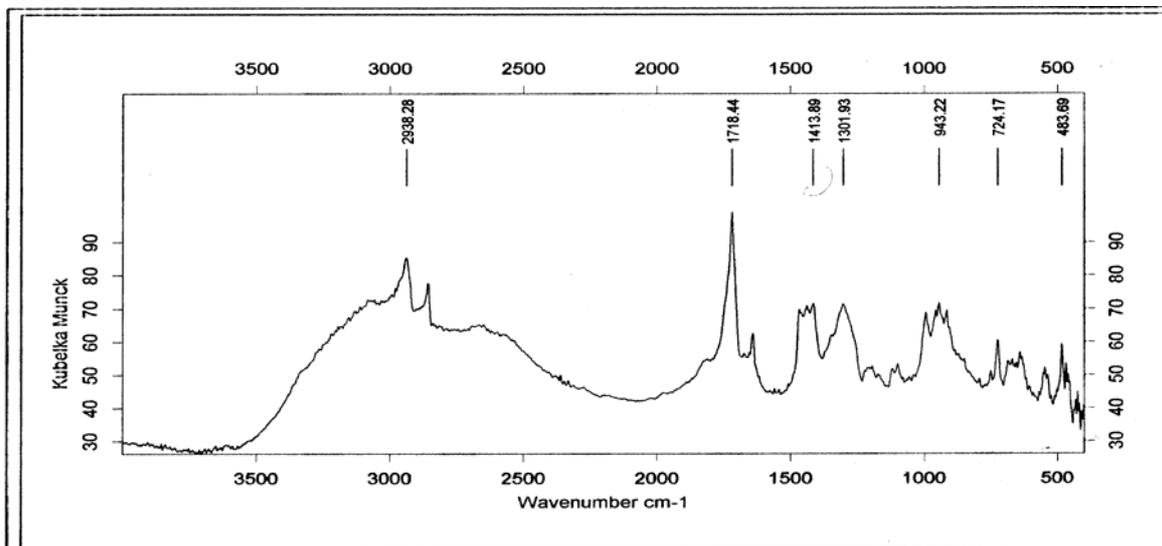


Figure 4. Free 10-undecenoic acids FTIR spectrum

However, thermogravimetry evidenced the surface area covered with unsaturated acid, which can be calculated from weight loss at 250-350 °C (fig. 5).

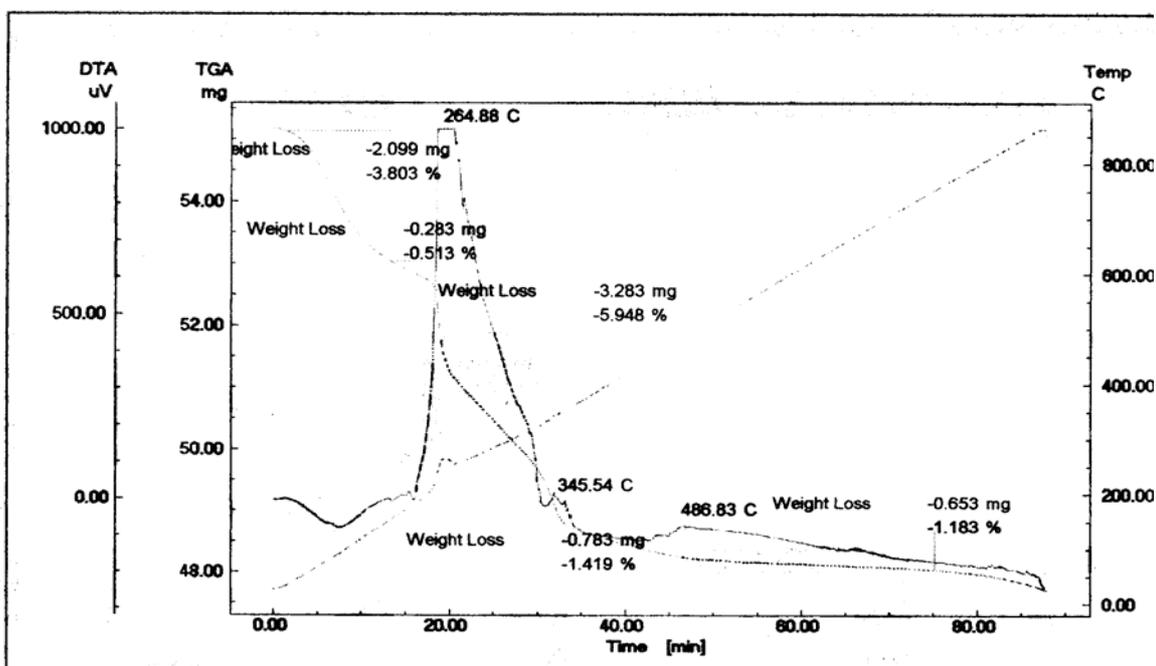


Figure 5. Thermogravimetry of magnetic particles covered with 10-undecenoic acids

These results agree with other works [9, 10] and suggest some application of double bonds in grafting of organic or inorganic compounds.

### **Conclusions**

A new ferrofluids based on tributylphosphate and magnetite was presented and some aspects of surfactants covered were evidenced.

### **References**

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*This work was partially supported on RELANSIN project no 1684.*