Oxidation Resistance of Iron-Based Magnetic Nanoparticle Fluids Prepared by Inert-Gas Condensation

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Motivation

Magnetic fluids have many biomedical applications

- Hyperthermia
- Targeted drug delivery
- Magnetic imaging
- Gene delivery
- Cell isolation/sorting
- Purification

Requirements

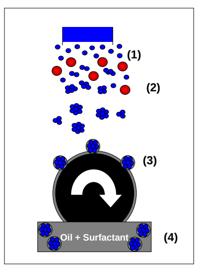
- Biocompatibility
- Choice of mean particle size
- Stability as a suspension
- Choice of materials
- Phagocyte resistant
- Narrow size distribution
- Oxidation resistance
- Functionalizable

Inert-gas condensation into liquids

- UHV Based
- Narrow size distribution
- 5-50 nm mean size
- Choice of surfactant

Deposit any sputterable or evaporable material including alloys, oxides and nitrides

Sample Preparation



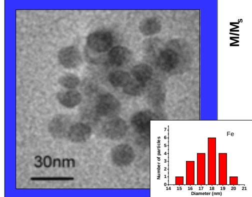
- Sputtering gun forms vapor (1)
- Vapor atoms collide with inert gas, forming clusters (2)
- Clusters are deposited on a rotating drum (3) coated with oil and a surfactant (4)

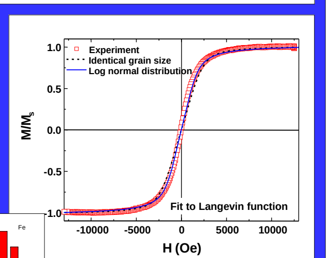
- UHV-based technique
- Any 'sputterable' material can be studied
- Good control over cluster size and size distribution
- Flexibility to deposit multiple materials simultaneously

Morphology and Magnetic Properties

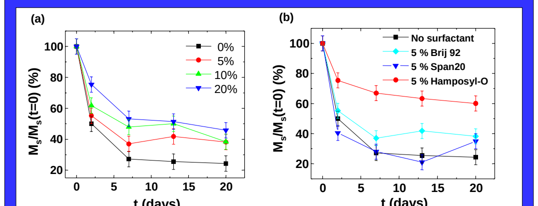
Iron Fluids

Mean size: 11.6 nm
Dist. Breadth: σ = 2.2 nm
Fluid: Octoil
Surfactant: Brij-92 (5 vol. %)
M_s = 87.5 emu/g_{Fe}

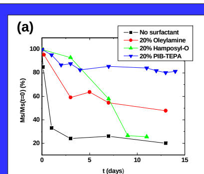


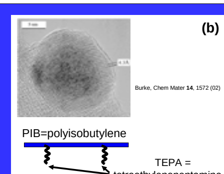


Oxidation Resistance



Decay of saturation magnetization as a function of time in air for (a) varying percentages of Brij 92 and (b) three different surfactants. All samples are volume percent surfactant in Octoil.





(a) Decay of saturation magnetization as a function of time in air. The sample with 20% PIB-TEPA shows the minimum decrease in saturation magnetization (10%). (b) Schematic structure of PIB-TEPA and TEM of a PIB-TEPA-coated particle.

Oxidation Resistance

Factors causing oxidation of nanoparticle fluids

- Diffusion of oxygen through carrier liquid
- Oxygen in carrier liquid
- Oxygen in surfactant

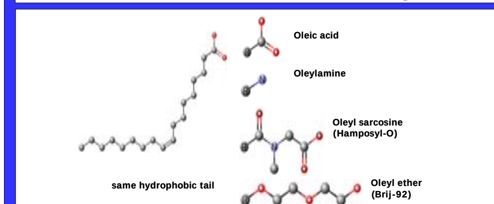
Surfactant features governing its capability for oxidation resistance

- Hydrophilic-Lipophilic Balance (HLB)
- Charge of the hydrophilic (polar) head-group
- Conformation
- Branching / Saturation
- Surface area occupied
- Type of bonding to particle
- Viscosity
- Packing of surfactant molecules on the particle surface
- Strength of chemical bonding between the particle surface and surfactant molecules

Why Amine-Based Surfactants…(Oleylamine, PIB-TEPA)?

- *Positive charge, stronger bonds with usually negative particle surfaces*
- *Better tendency to combine with longer aliphatic polymer chains*
  - *Better hydrophobicity*
  - *Closer packing*
  - *Lower chances of O_2 diffusion into the interfaces*
  - *Better miscibility in non-polar organic solvents*

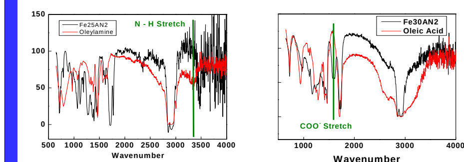
Surfactants – *Structure, Properties*



Name	HLB	MW	Charge	η (mPa s)
Hamposyl-O	10	270	Amphoteric (anionic in oil)	300
Oleylamine	8	268	Cationic	12
Brij-92	5	356	Non-ionic	unknown
Oleic acid	1	282	Anionic	26

Oxidation Resistance

Conclusions from Fourier Transform – Infrared Measurements



Oleic acid, oleylamine show strong chemical bonding with the particle surface ⇒ *good oxidation resistance*
Hamposyl-O is weakly bonded to the particle surface ⇒ *poor oxidation resistance*

Conclusions

- Inert-gas condensation into liquids
  - Fe, Co and Fe-N fluids
  - Mean particle sizes from 5 - 50 nm
  - Narrow size distribution
  - Broad materials choices possible
- Surfactant choice affects oxidation of Fe fluids
  - Particles with PIB-TEPA surfactant show the minimum decay of magnetization with time ⇒ *better oxidation resistance*
- All fluids highly stable for long periods of time
- Oil-to-Water phase transfer studies on Fe fluids
  - Particles capped with viscous surfactants such as PIB-TEPA tend to separate well from oil medium when treated with polar organic solvents such as aliphatic alcohols
  - ⇒ *Essential for TEM characterization, biological applications*
  - ⇒ *Further studies in progress*

Future Directions

- Explore more effective techniques for phase transfer and particle dispersion
- Bio-compatibility studies on PIB-TEPA
- Higher moment particles: *optimized synthesis protocols, use of better bio-compatible surfactants that would offer better oxidation resistance*
- MRI contrast agent studies
- Delivery of hydrophobic drugs

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