IRON COLLOIDS PREPARED BY CHEMICAL LIQUID DEPOSITION

GALO CÁRDENAS T* AND VIVIANA DELGADO G.

Departamento de Polímeros, Facultad de Ciencias Químicas,
Universidad de Concepción, Concepción (Chile).

(Received: April 14, 2009 - Accepted: August 15, 2009)

ABSTRACT

Iron colloids were prepared by cocondensation of the metal at 77K with ethanol, 2-propanol and 2-methoxyethanol. The distribution of particle sizes was determined by transmission electron microscopy.

The particle size of the colloidal dispersions ranges from 3.94 nm for Fe-ethanol and 6.70 nm for Fe-methoxyethanol. Electron diffraction was carried out for Fe-2-propanol colloids and exhibit the presence of FeO.

Electrophoretic measurements such as colloid charge and zeta potential were achieved. It was found that the colloids possess electrical charge, therefore it is postulated that their stability is by simple solvation. The colloids showed very high stability at room temperature, being over 30 days.

In some colloids absorption bands in the UV region were observed. A band at 201 nm and the band at 320 nm is due to the absorption of metal-metal. In the visible region no plasma absorption was found.

Keywords: A. Nanostructures; A. colloids; microscopy; C. infrared microscopy; B. vapor deposition; C. electron microscopy; D. infrared microscopy.

INTRODUCTION

The colloidal chemistry research is becoming more interested in material science. The application of these new materials exhibit a great variety including several fields of science, paints and colorant industries, medicine, agronomic chemistry, heterogeneous catalysis, photography and nanotechnology.

The colloidal chemistry is performed by homogeneous systems, where one or more components present dimensions ranging from micrometers to nanometers, somehow we are involved between macromolecules and very small particles^{1,2}.

The mechanical and chemical properties are very different to the properties of the same system but with bigger sizes. Also it has been found that new materials can be prepared by the control of particle size. The modification in size involves the different properties such as electrical, magnetic, optical and chemical.

The magnetic colloids (ferrofluids) have been extensively investigated^{3,4}. magnetite particles (Fe_3O_4) have been studied because their synthesis is well known⁵. Their polydispersity is around 25 % and their particle size is limited.

On the other hand, metallic magnetic particles can be obtained in several sizes, with the advantage of a larger magnetic moment compared to iron oxides.

But a more convenient method is the thermal decomposition of metal carbonyl compounds which produces spherical particles after release of carbon monoxide.

Colloid iron particles were prepared by Griffiths et al⁶, they studied iron particles in several solvents using different stabilizing polymers and their oxidation behavior. More recently, Pathmamanoharan⁷ et al reported results on the synthesis and characterization of iron particles stabilized with modified polyisobutylene (PIB) and oleic acid in decaline.

Colloid of ferromagnetic materials are of special interest due to their technological applications as ferrofluids^{8,9}. The magnetic fluids find uses in data storage media, magnetic refrigeration, audio reproduction and magnetic sealing^{10,11}. Most commercial magnetic fluids are generally produced by grinding of magnetite (Fe_3O_4) in ball mills for several days in the presence of surfactants, which produces a broad particle size distribution¹². Chemical methods such as thermolysis of organometallic compounds and metal evaporation have also been applied to produce colloids of ferromagnetic materials^{13,14}.

Iron nanoparticles by CLD method were obtained^{15,16}. The clusters were prepared by resistive evaporation of metallic iron, followed by a fast cocondensation at 77 K with several organic solvents (ethanol, 2-propanol and 2-methoxyethanol). Nanocolloid are obtained and by solvent evaporation active nanopowders are prepared. The great advantage of this methodology is the control of particles, under the same conditions, free of interferents.

EXPERIMENTAL

Preparation Of Metal Colloids

The metal atom reactor has been already described^{12,13} as a typical example, an alumina-tungsten crucible was charged with 0.152g. of Fe metal

(lumps). Dry 2-methoxyethanol was placed in a ligand inlet tube and freeze-pump-thaw degassed with several cycles. The reactor was pumped down to 0.008 mbar while the crucible was warmed to red heat. A liquid nitrogen filled Dewar was placed around the vessel and Fe and 2-methoxyethanol (70 mL) were deposited over 1 h using 35 A. The matrix was a blue/purple color at the end of the deposition. The matrix was allowed to warm slowly under vacuum by removal of the liquid nitrogen Dewar for 1 h, upon meltdown a brown colloid was obtained. After addition of nitrogen up to 1 atm, the colloid was allowed to warm for another 0.5 h at room temperature. The solution was syphoned out under nitrogen into a flask ware. Based on metal evaporated and acetone inlet the molarity in metal could be calculated. Several concentrations were prepared under the same conditions. No presence of hydrogen evolved during the metal evaporation was observed. The vacuum remains constant during the evaporation.

The film was obtained by stripping the solvent under vacuum. The solvent evaporation on a substrate can be speeded by a N_2 flow or by using a warm substrate.

Electron Microscopy Studies

Transmission electron micrograph was obtained on a JEOL JEM 1200 EX 11 with 4 Å resolution by using copper grids coated with carbon foil. A drop of the colloid was placed on a copper grid and allowed it to dry.

Thermogravimetric Analysis

A Perkin-Elmer Model TGA-7 thermogravimetric system, with a microprocessor driven temperature control unit and TA data station was used. The sample weight was recorded and generally ranged between 5-10 mg. The sample was placed in the balance system and the temperature was raised from 25 to 550°C at a heating rate of 10°C/min. The sample weight was continuously recorded as a function of temperature.

Infrared Studies

Infrared Spectra was obtained using a Nicolet 5PC Spectrometer. KBr pellets were made for all the films. Spectra were recorded at a resolution of 2 cm^{-1} and a minimum of 128 scans accumulation.

Differential Scanning Calorimetry (Dsc)

A Polymer Laboratory Simultaneous Thermal Analyzer STA 625 (TGA-DSC) was used. The transition energy was proportional to the area under the peak and the DH for the film were obtained.

Uv-Vis Spectroscopy

A Perkin-Elmer 2100 Spectrophotometer was used. The solvent was employed as a reference, the sample spectra between 200 and 800 nm was recorded.

Zeta Potential

A Laser Zee Meter Model 501, Pen Kem was used. The charge and zeta

potential of the colloid were measured. Also it was compared with a Burton tube (0.25 m of length) measurement.

Statistical Analysis

An average of one hundred particles were counted in each micrograph. The histograms were obtained using the Origin 6 program.

RESULTS AND DISCUSSION

The metal is evaporated at low vacuum and simultaneously cocondensed with an organic solvent compound steam on the cold surface of a reactor. During the warm up process of the matrix they form small "cluster" of metals codeposited to 77K, with an excess of solvent, weak complex properties, the formation of metal-metal bond is favored and takes place the formation of small dispersed amorphous particles in the organic solvent¹⁷.

The particles size depends on the solvent and the used metal.

The stability of the dispersions formed by cocondensation of metallic atoms and vapors of organic solvent (to 77K), extends hours, days, weeks and even per years¹⁸. For each solvent the stability depends on the oxidation potential of the metal and for a given metal on the solvent used.

The Fe colloids were obtained by different simultaneous cocondensation of the metal with organic such as: ethanol, 2-propanol and 2-methoxyethanol. These solvents were added in excess with the idea to maintain the agglomerate ones or solvated metal cluster.

Solvents : Ethanol, 2- propanol, 2- methoxyethanol

Colloidal Dispersions.

Stability

For the obtained colloidal dispersions their kinetic stability was moderate, in terms of their flocculation power at room temperature. In table I the stability measurements for each one of the prepared concentrations are summarized¹⁹.

Table I. Fe metal colloids stability in organic solvent.

Solvent	Fe M*10 ⁻³	Stability	Color
2-methoxyethanol	1.0	> 30	Light Brown
	2.3	> 30	
	3.8	> 30	
2-propanol	1.1	> 30	Dark Brown
	2.2	> 30	
	3.5	> 30	
2-ethanol	1.1	> 30	Light Brown
	2.2	> 30	
	3.7	> 30	

The great stability of these systems probably must be due to the presence of group - OH, forming stable interactions with the metal²⁰.

In addition, when analyzing these results, we can conclude that the Fe metallic dispersions are quite stable in the organic solvents used, demonstrating that a strong solvation on them exist.

An important point is related with the influence of the stability and the concentration, showing a greater stability for the more diluted colloidal dispersions, this fact is attributed to that a smaller energy is needed so that the particles dispersed in the reaction media exhibit Brownian behavior.

Besides, it is observed that the obtained colloidal dispersions with 2-methoxyethanol have the greater stability with respect to the others, this can be due to their polarity or to the formation of some type of bonds or interactions with the metal surfaces.

Particle Size Studies.

The particle size was obtained through the analysis of micrographs, which show the presence of agglomerates dispersed on the grid. The optical measures of the diameters of particle population randomly selected, were represented in

a histogram which will provide information to us in distribution of the particle size. On the other hand, the adjustment of the normal curve reveals the average size; also to the Gaussian curves and the standard deviations for each average particle size were obtained.

In table II, are the obtained particle sizes for the colloidal dispersions of lower concentration, since when this parameter is increased it is not possible to visualize single nanoparticles. The agglomerates are very difficult to analyze, due to the low resolution of the equipment used. Sizes between 3.94 and 6.7 nm are observed, values that agree with the range of colloidal particles previously reported²¹.

Figure 1 shows the micrographs obtained by TEM and the respective histograms for prepared colloidal dispersions.

Fig. 1. TEM of Fe-2-methoxyethanol colloidal dispersion.

Table II. Particle size of colloid dispersions.

Solvent	Concentration Fe (Mx10 ⁻³)	Particle size (nm)
2-methoxyethanol	1.0	6.70
ethanol	1.1	3.94
2-propanol	1.0	4.75

Electron Diffraction

The patterns of electron diffraction of Fe metallic particles were taken from the Microscope Jeol JEM EX- 1200 and the results are shown in figure 2 and table III. The micro electron diffraction exhibits a ring pattern width d spacing of 2.177 Å° corresponding to the (2 00) line of iron oxide FeO. From table of standards the spacing for FeO correspond to 2.153 Å°.

Fig. 2. Electron diffraction pattern.

Table III. Electron diffraction data.

Dispersion	Diameter	D_{hkl} (Å)	hkl	phase	Data from table (Å)
Fe-2-propanol	1.9332	2.177	(2 0 0)	FeO	2.151

On the other hand, Suslick reported the sonochemical decomposition of $\text{Fe}(\text{CO})_5$ in the presence of a stabilizer to obtain a nanosized iron colloid. By TEM the iron particle in the polymer matrix ranges from 3 to 8 nm. These particles are rather amorphous.

Oleic acid was used as a colloid stabilizer ¹², the $\text{Fe}(\text{CO})_5$ treated with oleic acid was sonicated at 30°C for 1h and pseudo spherical particles of 8 nm were obtained.

In our system of Fe-ethanol, Fe-2-propanol and Fe-2-methoxyethanol average particle size ranging from 3.9 to 6.7 nm were prepared.

Electrophoresis.

This experiment was carried out for Fe-2-methoxyethanol of 1×10^{-3} M. With the electrophoretic mobility measures, the rate of migration was obtained. The equation of Debye-Huckel was used to calculate the respective potentials zeta (ζ) of the metallic dispersions.

Table IV shows the electrophoretic parameters, such as rate of migration (v), electrophoretic mobility (m_E) and zeta potential (ζ) of the dispersions and their loads.

Table IV. Electrophoretic parameters of Fe colloids.

Solvent	Concentration ($\text{M} \times 10^{-3}$)	v (m/ $\text{s} \times 10^{-6}$)	u_E ($\text{m}^2 \text{v}^{-1} \text{s}^{-1} \times 10^{-9}$)	ζ (V)	Electric charge
2-methoxyethanol	1.20	3.89	3.42	55.68	Positive
2-propanol	1.30	6.26	3.87	86.85	Negative
ethanol	1.03	1.11	9.26	77.45	Positive

UV-Vis Studies.

The spectroscopic measures of the colloidal dispersions with the lower concentrations was carried out. The measures of UV-Vis for Fe-ethanol show two absorption bands at 201 and 320 nm which are in agreement with the theoretical values calculated by Creighton ²² (see figure III). The band at 320 nm is related to the metal-solvent interaction.

Fig. 3. UV-Vis of Fe-Ethanol.

ACKNOWLEDGMENTS

The authors would like to thank the financial support of Fondecyt (Grant # 1080704) and to Cipa-Chile.

REFERENCES

- D.J. Shaw, "Introduction to Colloid and Surface Chemistry", Butterworth Heinemann, Fourth Edition, **1992**.
- B. Jirgensons and M. Straumanis, "Compendio de Química Coloidal", Compañía Editorial Continental S.A., **1965**.
- S.A. Papell, in: *U.S. Patent*, vol. 3, **1965**, p. 215.
- R.E. Rosensweig, *Ferrohydrodynamics*, Cambridge Univ. Press, Cambridge, **1985**.
- R. Massart, *IEEE Trans. Magn.* MAG-17 **1247** (1981).
- C.H. Griffiths, M.P. O'Horo, T.W. Smith, *J. Appl. Phys.* **50**, 7108 (1979).
- C. Pathmamanoharan, N.L. Zuiverloon, A.P. Philipse, *Prog. Colloid Polym. Sci.* **141**, 115 (2000).
- Fertman, V. E. *Magnetic Fluids Guidebook: Properties and Applications*; Hemisphere Publishing Co. New York, **1990**.
- Berkovsky, B. M.; Medvedev, V. F.; Krakov, M.S. *Magnetic Fluids: Engineering Applications*; Oxford University Press: Oxford, **1993**.
- Raj, K.; Moskowitz, R. J. *Magn. Magn. Mater.* **1990**, 85, 233.
- Charles, S. W.; Popplewell, J. *IEEE Trans. Magn.* **1980**, Mag-16, 172.
- Fertman, V. E. *Magnetic Fluids Guidebook: Properties and Applications*; Hemisphere Publishing Co.: New York, **1990**.
- Smith, T. W.; Wychick, D. J. *Phys. Chem.* **1980**, 84, 1621.
- Hoon, S. R.; Kilmer, M.; Russell, G. J.; Tanner, B. K. *J. Magn. Magn. Mater.* **1983**, 39, 107.
- K. Klabunde, "Chemistry of Free Atoms and Particles" Academic Press Inc. (1980).
- (J. Blackborow and D. Young, "Metal Vapour Synthesis in Organometallic Chemistry", Springer-Verlag, pag. 14-16, (1979).
- K. Klabunde and T. Murdock, *J. Org. Chem.*, **44**, 3901 (1979).
- G. Cárdenas and R. Oliva, *Eur. J. Solid state Inorg. Chem.*, **t.33**, 1135 (1996).
- S. Salinas and G. Cardenas. "Síntesis y Caracterización de Dispersiones Coloidales y Sólidos Bimetálicos Pd-Sn" (2003).
- G. Cárdenas, J. Acuña, V. Delgado and C.A.S. Lima, *J. Chil. Chem. Soc.* (49, xx, 2005).
- G. Cárdenas and R. Oliva, *Bol. Soc. Chil. Quím.*, **38**, 301-308 (1993).
- Creighton J.A, *J. Chem. Soc. Faraday. Trans.*, **87**, 3881 (1991).