SYNTHESIS AND CHARACTERIZATION OF GADOLINIUM COLLOIDS IN 2-METHOXYETHANOL

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ABSTRACT

Gadolinium colloids have been prepared by Chemical Liquid Deposition (CLD). The metal is cocondensed with 2-methoxyethanol to yield solvated metal atoms at liquid nitrogen temperature and upon warming stable liquid colloids are formed with several ranges of particle size depending on the amount of metal used. Zeta potentials (ξ) were calculated according to the convention of Hunter and the Hückel equation, for most of these negatively charged particles. Upon solvent removal, colloidal particles coalesce to form active solids, which contain some residual solvent. The synthesis of colloids and active solids from Gd with 2-methoxyethanol is reported. Transmission Electron Microscopy (TEM) allows us to determine particle size ranging from 20 to 30 nm. The UV-vis studies of the metal colloids reveals absorption bands at 241 and 298 nm. This studies indicate that organic solvents are solvating metal clusters.

INTRODUCTION

The lanthanides are element that posses f electrons and enough shielded by the external shields. Therefore, their properties are different from the first row transition metals, related with a contact with the medium and chemical reactions [1], if we consider the interesting properties of the lanthanides such as luminescence [2], reactivity [3,4], conductivity [5] and magnetism [6]. Our group has already synthesized Yb, Er and Pr colloids and fine powders by cocondensation of the metals with 2-propanol and 2-butane at 77 K [7].

The chelates of some lanthanides such as Eu²⁺, Tb³⁺, Dy³⁺ and Sm³⁺ have quite unique fluorescence properties among the large Stoke’s shift, sharp emission peaks, and long decay times. If the temporal discrimination is used to eliminate background and improve assay sensitivity. The combination of spectral and temporal resolution has been used in development of multiparametric assays.

The development of stable and fluorescent lanthanide chelates has been the homogeneous time-resolved fluorescence energy transfer and fluorescence quenching assays. The limited attention to spectroscopic studies to Gd³⁺ ion is due to the fact that all the transitions in the absorption spectrum are in the ultraviolet above 52000 cm⁻¹ (8,9).

Several hosts for Gd⁴⁺ mainly restricted to heavy metal fluoride glasses, their UV cut-off at wavelengths lower than 250 nm. Alonso et al. (10) studied the optical absorption spectrum of Gd⁴⁺ ions in the fluorozirconate glasses ZBLA and ZBLALi. Most of the transitions start from S₂ ground state of the 4f configuration of Gd⁴⁺. The excited terms which could be observed are P, D and Σ. We became interested in the synthesis of Gd colloids using polar solvents using the codeposition technique at low temperature.

EXPERIMENTAL

METAL COLLOIDS

A typical cocondensation was carried out using the equipment specially designed, previously reported [11-14]. An alumina tungsten crucible was charged with around 0.00861 g of Gd metal in lumps. Distilled and dried solvent (e.g., 100 ml) were placed in a ligand inlet tube and freeze-pump-thaw degassed for five cycles. The reactor was pumped to 1x10⁻⁷ torr, while the crucible was warmed to red heat. The temperature in the crucible at red heat should be at the boiling point of Gd (around 3266 °C). A liquid nitrogen filled Dewar was placed around the vessel and Gd (3.87x10⁻⁴ mmoles) and 2-methoxyethanol (60 ml) were codeposited over a 1.5 h period at rate of 0.67 mL/min, approximately. The matrix was a colorless at the end codeposition. The matrix was allowed to warm slowly for 1.0 h to room temperature under vacuum by removal of the liquid nitrogen Dewar. Upon meltdown, a colorless dispersion was allowed to warm for another 0.5 h to room temperature. The sol was siphoned into a flask under nitrogen flow. Based on the amount of solvent consumed, the concentration of the colloid could be calculated.

ELECTRON MICROSCOPY STUDIES

Transmission electron micrographs were obtained with a JEOL JEM 1200 EX II with 4 Å resolution, using copper grids with carbon foil. A drop of the colloid was placed on a 150-mesh copper grid and allowed to dry. Electron diffraction was also carried out. In this case, the micrographs were obtained using 120kV; 60 cm; K: 4.209 cm Å. The calibration was carried out with Au film (Aldrich Chemical, 99.99%) evaporated over a copper grid.

UV-VIS SPECTROSCOOPY

The UV absorption spectra of the colloids were measured at 25 °C in a Specronic Genesis 2 Spectrophotometer, using quartz cells. The background was set up with the proper solvent and each colloidal dispersion was examined.

ELECTROPHORETIC PROPERTIES

The charge of particles were measured in a Burton’s tube and later corroborated with a Zeta meter 3.0.

INFRARED STUDIES

Infrared Spectra was obtained using a Nicolet Magna 550 Model Spectrometer. KBr pellets were made for all the powders. Spectra were recorded at a resolution of 2 cm⁻¹ and a minimum of 128 accumulation. Far FTIR Spectra was obtained using a Nicolet Nexus Model Spectrometer. Polyethylene pellets were made for all the powders. Spectra were recorded at a resolution of 2 cm⁻¹ and a minimum of 550 accumulation.

THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric measurements of the active solids were carried out using a Perkin-Elmer TGA-7 model with a microprocessor for the temperature control. The weights of the samples were usually in the range of 5-10 mg. The aluminium sample pan was heated from 25 to 600 °C at a heating rate of 10⁰/min under nitrogen atmosphere.

RESULTS AND DISCUSSION

The gadolinium colloids were obtained by means of CLD method. The stability of the colloids is closely related to the intrinsic nature of the solvent. The characteristics of the solvent that the colloid stability promotes are: viscosity, dielectric constant and the tendency to establish interactions between the free electron pairs of the solvent with the metal.

The following figure 1 summarizes de synthesis of the gadolinium colloid using the methodology already described.
TRANSMISSION ELECTRON MICROSCOPY

TEM results were used to determine the average particle size of the particles. The Gd/2-methoxyethanol colloids exhibit a particle size ranging from 20 to 30 nm.

The 6.45 x 10^{-4} M dispersion exhibit a particle size of 18 nm. The value as large as particle reflects the stability of the colloidal system, since when the particles have a small size its thermodynamic stability is very low and they are aggregates to obtain a higher stability.

We postulate that the particles grow due to two factors. The first one must be related to a type of steric stabilization, the molecules of solvent are able to move and to rearrange on the surface of the metallic clusters and others are clustering due to chemical interaction. When clusters tend to be more massive, the kinetic energy decreases, and perhaps the energetic need of solvent due to the displacement and the rearrangement is translated in a greater particle formation.

A second possibility is the electronic affinity that the particles exhibit and allows them to acquire electrons from the walls of the reactor, the electrodes and most important of all of them, the subtraction of electrons of the solvent used to form the colloidal matrix at low temperature.

ELECTROPHORETIC PROPERTIES

The colloidal particles exhibits a negative charge which might be similar to previous colloids of Pr, Yb and Er previously reported (16,17).

UV-VIS SPECTROPHOTOMETRY

The kinetics of clustering was followed at room temperature, by taking absorption spectra every hour for 72 h. The stability of the colloid depends proportionally of the metal concentration in the matrix, since a dilute solution (6.45 x 10^{-4} M) does not produce a measurable increase of the absorbance due to the cluster growing and a later decrease due to flocculation.

Several UV spectra for lanthanides were reported, they were calculated by Creighton and Eadon by using the Mie approximation methods [18,19]. By comparison between the theoretical calculated spectra by the Mie approximation and compared with the experimental of the Gd in 2-methoxyethanol colloid, it can be observe the rising of two new bands. These ester bands exhibit variation in absorbance nor shift to the red or blue of the UV range. A sharp intense band appears at 241 nm, corresponding to the interband transition (transition 4f^7 → 5 d^1). A wider second band of lower intensity appears at 298 nm and is attributed to a plasmon resonance a typical metallic behavior (see figure 4).

ELECTRON DIFFRACTION

The electron diffraction analysis of the Gd/2-methoxyethanol of 6.45 x 10^{-4} M exhibit the present phases in the sample corresponding to Gd and GdO_3 with hkl (203) and (110) planes, respectively (15).

The pattern is not very clear (Fig. 3), since the forms of the ring exhibit lower intensity. On the other hand, it can be deduced that the sample posses low crystalline phases because they do not appear characteristic dots of crystalline systems.

Figure 1: Several stages to produce the colloid and the active solid of Gadolinium.

Figure 2: (a) Gd/2-methoxyethanol (6.45 x 10^{-4} M) TEM at dark field (100K) and (b) the corresponding histogram. Particle size, mean = 18.7 nm and SD = 7.3 nm.

Figure 3: Electron Diffraction pattern of Gd/2-methoxyethanol (6.45x10^{-4} M).

The following table summarizes the previous observations and is compared with tabulated values (15).

<table>
<thead>
<tr>
<th>Dispersion</th>
<th>Number of ring</th>
<th>Diameter (cm)</th>
<th>d_{exp} (Å)</th>
<th>d_{th} (Å)</th>
<th>(hkl)</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd in 2-methoxyethanol</td>
<td>1</td>
<td>2.136</td>
<td>1.970</td>
<td>1.932</td>
<td>(110)</td>
<td>GdO_3</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3.424</td>
<td>1.230</td>
<td>1.216</td>
<td>(203)</td>
<td>Gd</td>
</tr>
</tbody>
</table>

UV-VIS SPECTROPHOTOMETRY

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FTIR STUDIES
A medium and far FTIR was used. The KBr pellet exhibit characteristic bands of the solids powder of Gd/2-methoxyethanol shows the interaction of the cluster-solvent in the solid.

The following spectra (Fig. 5) it shows the characteristic bands found in the solids and that have been identified and compared with FTIR of the pure solvent (2-methoxyethanol). As we can see the $\nu_{\text{O-H}}$ is similar both solvent and solid (3429 and 3427 cm$^{-1}$, respectively). The $\nu_{\text{C-O}}$ exhibit bonds at 1069 and 1077 cm$^{-1}$ which is indicative of a low interaction between Gd and the carbonyl group. The shift of $\nu_{\text{O-H}}$ from 1189 to 1255 cm$^{-1}$ in the solid might be cause due to interaction with the Gd.

**Figure 5:** Medium FTIR of Gd/2-methoxyethanol active solid.

The Far IR show characteristic bands, metal-metal and metal-oxygen interaction (Fig. 6). The band at 221 and 133 cm$^{-1}$ correspond to symmetric and antisymmetric stretching Gd-Gd (20). The formation of metal-metal bonds was allowed since the CLD method promote it when the metal and solvent are codeposited at $-196^\circ\text{C}$. The form of the signal that appears to 384 cm$^{-1}$, it is possible to deduce that correspond to metal-oxygen stretching. There are several bands reported for Ti, Zr, Ta, Hf, Ta and Nb indicating the M-O stretching in a range between 540 and 420 cm$^{-1}$.

**Figure 7:** Far FTIR of Gd/2-Methoxyethanol active solid.

THERMOGRAMMETRIC ANALYSIS
The thermogravimetric studies allows us to find out the thermal stability of the active solids. The Gd/2-methoxyethanol exhibit a decomposition at 105.94 $^\circ\text{C}$ and the main decomposition at 549.25 $^\circ\text{C}$ with a total weight loss of 47.47 % very similar to Pr-2-butanone previously described (7), while Yb and Er showed a lower weight loss (34%). The greater weight loss of Pr is consistent with higher solvent incorporation.

**Figure 8:** Thermogram and DSC Analysis of active solid of Gd/2-methoxyethanol.

CONCLUSIONS
- It is possible to obtain colloids of Gd/2-methoxyethanol of low stability, by the CLD method at 77 K.
- The flocculation process of the particles occur at room temperature after 12 h due to the low stability of the colloid. The flocculation of the colloid was corroborated by the UV spectrum, the absorbance band decreases slowly after the time goes from $t = 0$ to $t = 12$ h.
- By FTIR probes that metal slow characteristic bands due to the metal-solvent interaction.
- The TGA shows the good thermal stability of the Gd/2-methoxyethanol.

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REFERENCES
5. A. Henglein, Colloid & Polymer Sci., 1987, 1, 73.6.