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ORIGINAL CONTRIBUTION

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Bismuth colloids and films from non-aqueous solvents

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Abstract Bismuth colloids and metal–metal oxide films have been prepared by the method Chemical Liquid Deposition (CLD). The metal is evaporated to yield atoms which are solvated at liquid nitrogen temperature, and upon warming stable liquid colloids, are formed with particle size ranging between 50–350 Å. Zeta potentials 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 films, which contain some residual solvent. The synthesis of colloids and films from Bi with acetone, 2-butanone, 4-methyl-2-pentanone, ethanol, 2-propanol, DMF, THF, DMSO, benzene and toluene is reported. Transmission Electron Microscopy (TEM) allows us to determine particle size. FTIR, Thermogravimetric Analyses (TGA) and Scanning Electron Microscopy (SEM) have aided in film characterization. These studies indicate that solvents are incorporated into the films. Resistivity studies showed that they behave as semiconductors rather than pure metals. TGA studies reveal that loss of weight occurs within 244–453 °C. The films are very stable with 5–30% weight loss at 550 °C.

Key words Metal colloids – metal particles – metal films – chemical liquid deposition

Introduction

Metal codeposition with organic solvents at 77 K produces several reactions [1]. Our interest has been in solvated metal atoms [2] in whose solutions the atoms are only "lightly stabilized". This solvation has been useful to obtain metal colloids that are stable at room temperature [3, 4]. The more stable metal colloids in organic solvents are based on the clustering of metal atoms at low temperature [5].

This approach is open to many metals or solvents and the resultant colloidal particles are free of interferences and impurities generally present in aqueous preparations.

The solvated metal atoms are interesting from another point of view. When the solvate decomposes, the atoms begin to cluster in the organic medium. This culstering process is affected by the organic solvents, the metal, concentration and temperature. Active powders and/or potential catalysts may be obtained.

The stabilization of colloidal particles is probably due to adsorption electrons or ions in the solution [6], along with protective ligation by residual solvent.

Another application of these colloidal systems is their tendency to form films upon solvent removal [7–10]. They can grow to films under mild conditions. These materials may have unusual optical and/or magnetic properties.

Several studies have been carried out on bismuth films as well as Te-, Sn- and Ga-doped polycrystalline films [11]. In donor-doped bismuth at higher temperatures, the consideration of the hole conduction is also required because of thermal excitation of holes.

In semi metals, according to Shik [12], band bending results in a redistribution of charge carriers of opposite signs producing a local decomposition over the inner and sub-surface regions of the film, whereas the carrier concentrations n and p averaged over the film remain compensated.

In this paper we demonstrate the synthesis of colloids and films with bismuth employing organic solvents.

Experimental

Preparation of Bi-THF colloid

The metal atom reactor used (3 L) has been described in previous reports [13, 14]. As an example, an alumina-tungsten crucible was charged with 0.25 g Bi metal. THF (150 g) just distilled and dried was placed in a ligand inlet tube and freeze-pump-thaw degassed with five cycles. The reactor was pumped to 1×10^{-4} Torr while the crucible was warmed to red heat. A liquid nitrogen filled Dewar was placed around the vessel and Bi (0.258 g) and THF (132 g) were codeposited over a 1 h period. The matrix was a black color at the end of the codeposition. The matrix was allowed to warm for 1.5 h to r.t. slowly under vacuum by removal of the liquid nitrogen Dewar. Upon meltdown, a black dispersion was obtained. After addition of nitrogen, up to 1 atm, the dispersion was allowed to warm for another 0.5 h to room temperature. The dispersion was siphoned out under nitrogen into a flask. Based on metal evaporated and THF used, the molarity in metal could be calculated. (Less than 5% of metal is deposited in the electrodes, so most of the metal is in the colloid).

Electrophoresis experiments

The electrophoresis experiments were carried out by using a glass U-tube of 11.0 cm with a stopcock on the base to connect a perpendicular glass tube (13 cm long × 35 cm high). Platinum electrodes were attached to the top of the U-tube and through a ground glass joint to the pole of a 15 V power supply. The 2-butanone was placed in the U-tube. A typical experiment was carried out for a period of 3 h at 25 °C.

Scanning electron microscopy studies (SEM)

Electron micrographs were obtained on a ETEC Autoscan U-1 Model and the films were coated with gold for 3 min to obtain a 150 Å thickness using a Edwards S 150 Sputter coater.

Transmission electron microscopy studies (TEM)

Electron micrograph were obtained on a JEOL JEM 1200 EX II with 4 Å resolution. A drop of the sample was placed on a carbon-coated copper grid of 100 mesh.

Elemental analysis

The samples for microanalysis were handled by our Microanalysis Laboratories in our Faculty of Chemical Sciences. The metal samples were determined by atomic absorption after previous acid treatment on a Perkin–Elmer 3100 Model. On the other hand, C, H, N and S were determined by using a Perkin–Elmer Elemental Analyzer 1200 Model.

Thermogravimetric

A Perkin–Elmer Model TGS-2 Thermogravimetric System, with a microprocessor driven temperature control unit and a TA data station, was used. The weights of these samples were recorded accurately and were generally in the range of 5–10 mg. The sample pan was placed in the balance system in the equipment and the temperature was raised from 25° to 550 °C at a heating rate of 10 °C min^{-1}. The weight of the sample was continuously recorded as a function of the temperature.

Infrared spectra (FTIR)

Infrared spectra were obtained using a Nicolet Magna 5PC Fourier Transform Infrared Spectrometer. KBr pellets were prepared for all the films. Spectra were recorded at a resolution of 2 cm^{-1}. One-hundred-and-twenty-eight scans were accumulated for each spectrum.

Solubility studies

The films were completely insoluble in several solvents: acetone, 2-butanone, 2-propanol, THF, DMSO, toluene and benzene. The films were tested for 24 h of contact under stirring at 25 °C.

Conductivity

By scrapping the films, the active powders were shapped in an IR pellet device to obtain 1 mm thickness and resistivity was measured. It was connected to electrodes at each end by vapor deposition on a pellet of copper.

A Keithley Power Supply Model 241 and an electrometer, Keithley Model 610 C, were used to measure conductivity. The metal covering was achieved by using an Edwards High Vacuum Ltd. Coating Unit Model 12 EA 1650.

Results and discussion

A series of black colloidal solutions using different solvents was prepared by using Scheme 1:

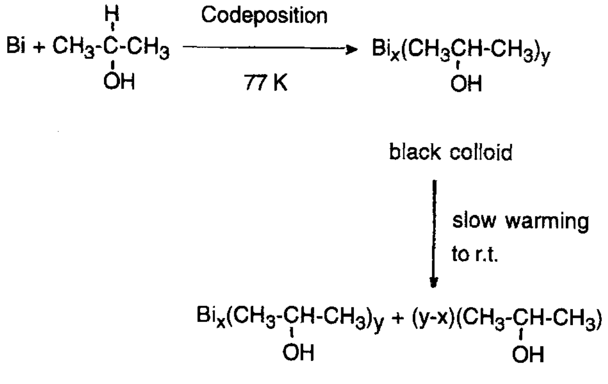
In order to establish the properties of these colloids, several measurements were carried out.

Colloidal bismuth studies

Electrophoresis

Most of the aqueous metallic colloidal particles carried negative charge [6a] and the rate of migration of these particles can be determined as the electrophoretic mobility (μE). For most of the colloids the velocity of migration was determined (see Table 1). Bi-ethanol and Bi-DMF colloids exhibit similar migration velocity due to their higher dielectric constants. However, for Bi-DMSO the migration was twice that of the others; this can be explained due to the higher D of DMSO. Of course, it is not easy to explain the difference between 2-butanone and ethanol since their dielectric constants are similar, however, it should be due to the higher viscosity of 2-butanone.

Scheme 1 Colloid bismuth formation



The zeta potentials were obtained using the Debye–Hückel equation [7]. The high values of zeta potentials are due to the charge density of these colloids. These values are in agreement with copper colloids reported previously [10].

Flocculation

It is known that electrolytes added to aqueous metal colloids produce the breakdown of the charged double layer, which allows particle flocculation. Several electrolytes were added to the Bi-colloidal sols in order to induce flocculation [19]. Three solutions, 0.01 M of Na^+, Ca^{2+} and Al^{3+} were prepared in acetone, respectively. Results are in agreement with data reported by Furlong [20] in which high-valent cations induced flocculation faster than monovalent cations. Flocculation of the colloid was observed after 5, 3 and 1 min, respectively.

Stability

In dilute solutions of atoms, the frequency of encounters will be lower. During the warming of the metal atom solvent matrix, the atoms and the particles become mobile, it is the number of encounters that occurs during the period before particle stabilization that becomes important. When metal concentration becomes higher, particle size becomes larger causing precipitation.

The more stable colloids occur in DMSO but ethanol, 2-propanol, THF and DMF exhibited some stability (see Table 1). However, the least stable colloids were Bi-acetone and Bi-4-methyl-2-pentanone. For alcohols, the stability decreases with increase in the aliphatic chain. The stabilities of colloids correlate well with the dielectric constant (*D*) of the solvents (DMSO and DMF have the highest *D* values and ethanol and 2-propanol have the lowest *D* values).

On the other hand, for ketones, due to their similar *D*, the difference appears to be due to their viscosities. The stability time until 50% of the sol flocculated was considered.

The electrophoresis experiments show that the Bi particles are negatively charged. It is clear that these negative charged particles will repel each other and therefore help their stabilization. Zeta potentials are indicative of substantial electronic stabilization. Most of the colloid showed electrophoretic mobilities around 10^{-8} ($m^2/V.s$). Aqueous colloids, e.g., colloid gold 3×10^{-6} ($m^2/V.s$) colloidal platinum 2×10^{-6} ($m^2/V.s$) (18). The zeta potential can be calculated according to the convention of Hunter (17) and the Hückel equation ($\mu E = 2\varepsilon_0 D\xi/3\eta$).

Table 1 Particle size, stability and zeta potentials of Bi colloids

Colloid	Conc. × 10^3 M	Size [Å]	Velocity migration (mm/h)[a]	Zeta potential (mV)	Stability[c] (h)
Bi-Acetone	5.33	67	b	b	2
Bi-2-butanone	8.40	133	4.0	−778	4
Bi-4-methyl-2-pentanone	11.50	67	b	–	1
Bi-DMF	9.30	133	2.0	−411	6
Bi-THF	8.00	50	–	b	6
Bi-DMSO	12.84	133	5.0	−2033	240
Bi-ethanol	8.71	67	2.0	−84	6
Bi-2-propanol	5.43	333	2.5	−32	2
Bi-benzene[d]	9.64	67	–	–	1
Bi-toluene[d]	9.54	350	–	–	1

[a] All the colloids are negatively charged.
[b] Flocculation during the experiment.
[c] Stability in hours.
[d] These more resemble dispersed metal than colloids.

Table 2 Composition of Bi thin films a)

Films	Concn. M (× 10^3)	% Bi	% C	%H b)
Bi-acetone	5.33	96.0	1.16	0.41
Bi-2-butanone	8.40	90.3	3.81	0.77
Bi-4-methyl-2-pentanone	11.50	88.4	3.20	0.42
Bi-DMF c)	9.30	74.7	18.97	2.08 (0.06)
Bi-THF	8.00	82.5	12.47	2.86
Bi-DMSO d)	12.84	96.1	2.03	0.47 (1.05)
Bi-ethanol	8.71	80.9	1.93	0.19
Bi-2-propanol	5.43	95.7	1.01	0.16
Bi-benzene e)	9.64	87.2	1.91	0.36
Bi-toluene e)	9.54	86.8	2.01	0.40

a) Microanalyses were obtained from Facultad de Ciencias Laboratories, Universidad de Concepción.
b) Oxygen is the most likely missing percentage.
c) In parentheses, nitrogen content.
d) In parentheses, sulphur content.
e) These powders derived from a non-colloid.

The magnitudes of zeta potentials are also consistent, the stability increases with the increase of ξ (DMSO is the most stable and 2-propanol the least stable).

Conductivity

The powders were pressed to get a pellet of 1 cm diameter and 1 mm thickness. Four silver dots were used to measure conductivity. The Bi-acetone sample exhibited a high conductivity ($1.7 \times 10^{-5} - 6.3 \times 10^{-6}\ \Omega \cdot \mathrm{m}$), their resistivity was similar to pure bismuth ($\rho = 1.07 \times 10^{-6}\ \Omega \cdot \mathrm{m}$).

Elemental analysis

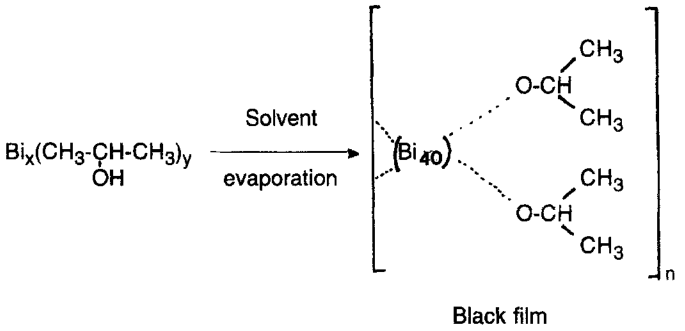
The Bi films were obtained after vacuum evaporation of solvent over a period of several hours at 10^{-3}–10^{-4} Torr (Scheme 2):

The colloids show a ratio of approximately $x/y = 1/2400$. Metal atoms are solvated in an excess of organic solvent.

Furthermore, substantial amounts of carbon and hydrogen remained attached or incorporated to the films (see Table 2). Most of the films exhibited a C/H ratio between 3 to 7. It is also interesting to note the presence of N and S in DMF and DMSO films, respectively. In the films the metal/solvent correlation becomes opposite to the colloids, with a ratio of Bi_{20} (C_3H_7O).

SEM and TEM studies

The sols were dripped on carbon-coated copper grids in such a way that solvent evaporation left particles. Our TEM micrograph of Bi-DMF colloid (Fig. 1) showed spherical particles of average size 133 Å. On the other



Scheme 2 Bismuth thin film formation

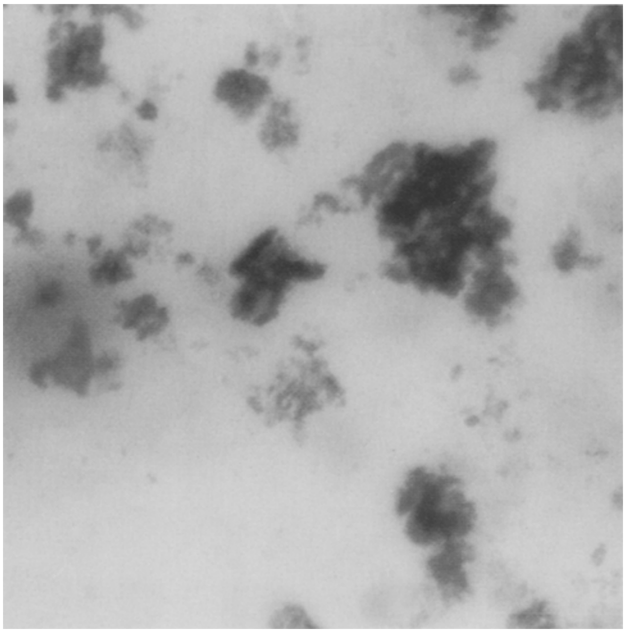


Fig. 1 TEM micrograph of Bi-DMF at 75 × 10^3 X

hand, Bi-4-methyl-2-pentanone colloid exhibited also spherical particles of average size 67 Å (see Fig. 2).

Scanning electron microscopy

SEM showed that the films formed by solvent evaporation on copper foils are made up of irregular surfaces such as with Bi-2-propanol. This morphology can be seen in Fig. 3.

Films of different thickness were prepared by dripping the colloidal solutions on a glass plate. The films are easily oxidized upon air exposure, producing a mixture of Bi and Bi_2O_3.

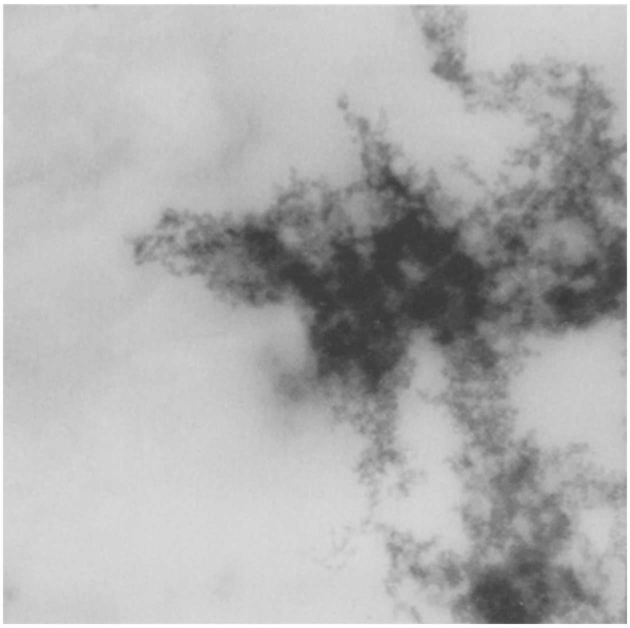


Fig. 2 TEM micrograph of Bi-4-methyl-2-pentanone at 75 × 10^3 X

Fig. 3 Scanning electron micrograph Bi-2-propanol, 5 × 10^3 X

FTIR

Infrared spectra of films derived from Bi-4-methyl-2-pentanone showed bands at 2960, 2933.3 and 2870.2 cm^{-1}

(ν_{C-H} corresponding to $-CH_3$,$-CH_2-$). A band at 1733 ($\nu_{C=O}$) and bands at 1122 and 1087 cm^{-1} (ν_{C-O}) are according to the structure of the solvent in the film. Bi-DMF film exhibited bands at 2933 and 2855 cm^{-1} (ν_{CH_3}) a band at 1425 cm^{-1} (ν_{C-N}) and at 1640 cm^{-1} ($\nu_{C=O}$ of amide) (Fig. 4b).

The Bi-THF film exhibited bands at 2966 cm^{-1} (ν_{C-H}) and 1097 and 1018 cm^{-1} (ν_{C-O}) [21]. Apparently, the solvents are incorporated into the films (Fig. 4a).

Thermal stabilities

Most of the films are very stable and they did not lose weight until 300 °C and around 15% of the total at 550 °C. In Table 3 are summarized the data from thermograms of these Bi films.

Bi-ethanol film is the more thermally stable film (453 °C) followed by Bi-DMF (401 °C). These values are similar to Sn films reported before [3] (Fig. 5).

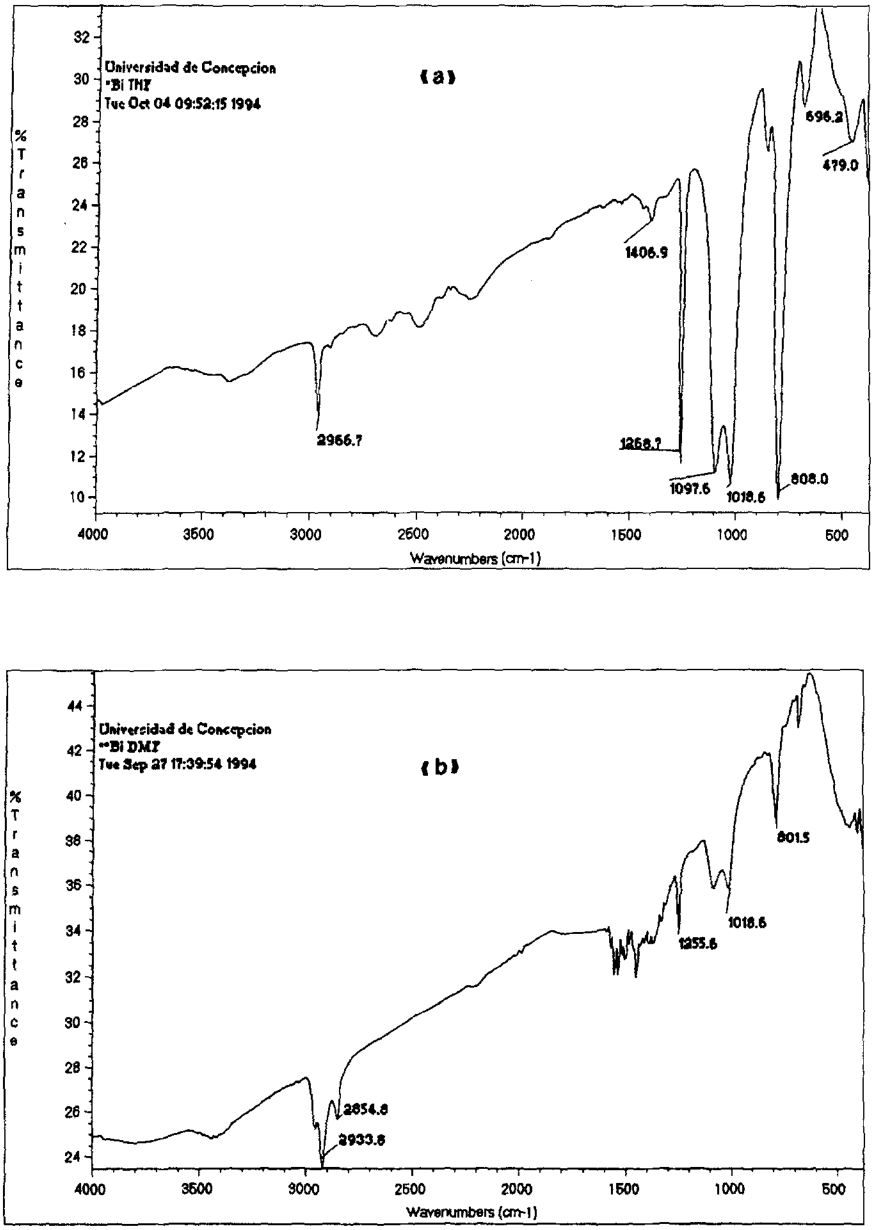


Fig. 4 FTIR of (a) Bi-THF and (b) Bi-DMF films

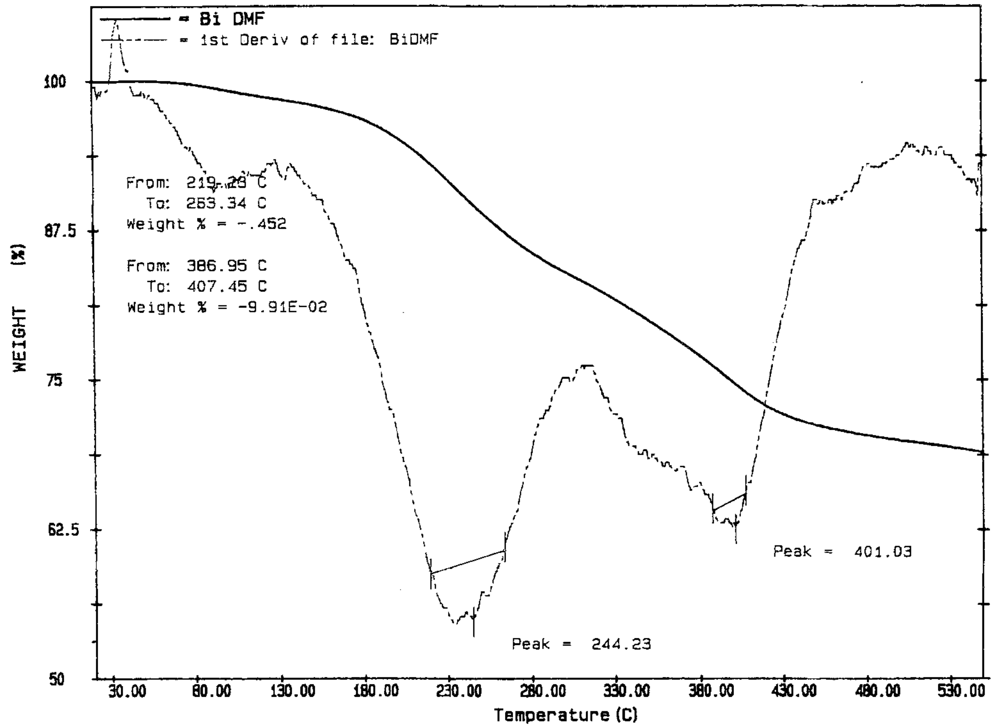


Fig. 5 Thermogravimetric curve of Bi-DMF film obtained by heating the sample from 25° to 550 °C at 10 °C·min^{-1}

Table 3 Thermal stability of Bi films

Films	Decomposition temperature (°C)/T_{D1})	T_{D2}	Weight[b] loss%
Bi-acetone	300		4.29
Bi-2-butanone	310		19.60
Bi-4-methyl-2-pentanone	263.98	395.20	6.02
Bi-DMF	244.23	401.03	30.10
Bi-THF	255.20		10.86
Bi-DMSO	a		a
Bi-ethanol	264.71	453.00	31.80
Bi-2-propanol	*		3.80
Bi-benzene	305		9.10
Bi-toluene	353.98		11.50

[a] No derivative was obtained.
$T_{D1,2}$ = decomposition temperatures.
[b] Maximum weight loss at 550 °C.

Bi-THF film is the least stable and decomposes at 255 °C. Only three films exhibited two decomposition temperatures. These values can be obtained from the first derivative from the thermogravimetric curves.

Conclusions

The most relevant fact was that most of Bi-colloids in organic solvents are spherical and negatively charged. The films, upon solvent removal, still contain organic residues. They exhibited conductivity similar to pure metal. Furthermore, these films can be obtained on several surfaces such as plastic, glass and metals by spraying the respective solutions. Also, it was possible to transfer the films to adhesive tape. It is difficult to get very homogeneous films free of oxidation.

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