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ORIGINAL CONTRIBUTION

G. Cárdenas
A. Ponce

Cadmium colloids from non-aqueous solvents

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Prof. Galo Cárdenas (✉) · Audaldo Ponce
Departamento de Polímeros
Facultad de Ciencias Químicas
Universidad de Concepción
Casilla 3-C
Concepción, Chile

Abstract Cadmium colloids have been prepared by 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 25–100 Å. Zeta potentials were calculated according to the conversion of Hunter and the Hückel equation, for ethanol and dimethyl sulphoxide. UV/VIS measurement of most of the black colloids showed absorption band around 280 nm. For comparison, we prepared CdS colloid with size 400–625 Å. The colloids are stable to oxidation in air and/or oxygen bubbling. The synthesis of colloids and films from Cd with acetone, 2-butanone, ethanol, 2-propanol, 2-methoxyethanol, DMF and DMSO is reported. Transmission Electron Microscopy (TEM) allows us to determine particle size.

Key words Metal colloids – cadmium atoms – chemical liquid deposition – particle size – absorption bands

Introduction

When free atoms of metals are allowed to deposit with organic solvents at low temperature, often a limited mode of atom agglomeration takes place [1–5]. Colloidal size metal particles are formed by metal atom migration and clustering. Nevertheless, growth stops due to a delicate balance of forces such as particle surface solvation, particle charging, and surface energy. Both steric and electronic effects should be considered.

In fact, aqueous colloidal solutions of gold, palladium and other metals have been known for centuries, and have undergone extensive study [6]. And, although much more rare, non-aqueous colloidal metals are also known [7]. But the current systems prepared by metal atom agglomeration under low temperature conditions are different from these previous systems in that no counter ions, reducing materials, or pyrolysis products are present – only metal particles and pure solvent [1–5, 8]. This difference results in a very important property for some metal-solvent combinations: with these metal particles, upon solvent removal or other manipulation, particle growth can occur [1–5].

Colloidal dispersions of metals exhibit absorption bands or broad regions of absorption in the UV-VIS range. These are due to the excitation of plasma resonances or interband transitions, and they are thus a very characteristic property of the metallic nature of the particles. Some colloidal metals have distinct absorption bands in the visible region, and as a consequence they have attractive colors. The most notable of these are dispersions of silver, copper and gold, which have applications as the yellow or red coloring agents in some colored glasses and in decorative glazes for porcelain. Colloidal particles of the alkali and alkaline-earth metals trapped in ionic crystals

[9,10] or inert-gas matrices [11,12] also have distinct absorption bands in the visible range, as do aqueous colloidal cadmium [13] and thallium [14].

Calculations by Creighton and Eadon have shown that cadmium particles in aqueous solution should absorb in a rather narrow wavelength range around 280 nm [15].

Henglein found a weak band at 260 nm for Cd ions reduced upon γ-irradiation [16]. We report that most of these Cd colloids in organic solvents exhibited absorption in the range of 210–290 nm depending upon the solvent.

Experimental

Preparation of Cd-2-methoxy ethanol colloid

The metal atom reactor used (3L) has been described in previous publications [17,18].

As an example, a tungsten crucible with a ceramic cup was charged with 0.30 g Cd metal. 2-Methoxy ethanol (60 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 Cd (0.10 g) and 2-methoxyethanol (50 mL) 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 2-methoxy ethanol used, the molarity in metal used could be calculated.

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 $\times$ 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 19 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.

Transmission electron microscopy studies (TEM)

Electron micrographs were obtained on a JEOL JEM 1200 EXII with 4 Å resolution. A drop of the sample was placed on a carbon coated copper grid of 100 mesh. Several magnifications were used ranging from 5.0×10^4 to 2.0×10^5. A log normal distribution to determine particle size was used.

Elemental analysis

The samples for microanalysis were handled by our Microanalysis Laboratories in our Faculty of Chemical Sciences. The metal samples were analyzed by atomic absorption after previous acid treatment on a Perkin–Elmer 3100 Model. In addition, 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 the samples were recorded accurately and were generally in the range of 5–10 mg. The Al 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.

UV/VIS

The absorption spectra were measured at 25 °C by using a Lange Spectral Photometer CADAS 100 using a 1 nm resolution.

CdS Colloid

The colloid was prepared in a 250 mL round bottomed flask with 50 mL solution of CdI_2 in DMSO 0.10 M. From another flask H_2S(g) was bubbled and dried in a trap with P_2O_5 [19].

The CdI_2 solution was degassed by bubbling N_2(g) for 1 h. Then, 70 mL of HCl 1 M were dropped over 2.5 g of

Na_2S over a 50-min period. The $H_2S(g)$ generated was carried with $N_2(g)$ and bubbled in CdI_2 solution. After 10 min, the samples for TEM and UV/VIS were taken.

Results and discussion

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

Scheme 1 Colloid cadmium formation

$$\underset{\text{atoms}}{Cd + xCH_3OCH_2CH_2OH} \xrightarrow[77\ K]{\text{Codeposition}} \underset{\text{black colloid}}{Cd_x(CH_3OCH_2CH_2OH)_y} \xrightarrow{\text{slow warming to r.t.}} Cd(CH_3OCH_2CH_2OH)_y + (y - x)\,[CH_3OCH_2CH_2OH]$$

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

Electrophoresis and stability

Most of the aqueous metallic colloidal particles carried negative charge and the rate of migration of these particles can be determined as the electrophoretic mobility (μE) [20]. For two colloids the velocity of migration was determined (see Table 1). Cd ethanol exhibits a high migration rate due to their smaller particle size (25 Å). Even though DMSO dielectric constant is twice that of ethanol, the slow migration rate is probably due to the larger particle size (50 Å) and also to the higher viscosity.

The zeta potentials were obtained using the Debye–Hückel equation [21]. The zeta potentials are higher than Pd and In colloids previously reported [21, 22] but similar to Bi colloids recently reported [23]. It is difficult to determine accurately the number of negative charges each particle possesses, it is evident that these negatively charged particles will repeat each other and therefore help their stabilization.

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 stability time was taken into account until the flocculation begun (see Table 1) showing stable sols for several months at r.t. The more stable colloids occur in DMSO and 2-methoxy ethanol.

The electrophoresis experiments show that the Cd particles are positively charged. Zeta potentials are indicative of substantial electronic stabilization.

The magnitude of zeta potentials is also consistent, the stability increases with smaller particle size.

Another interesting experiment was carried out, Cd-2-methoxyethanol colloid was bubbled with oxygen for 1 week at room temperature. No color change and/or flocculation was observed. Also, the particle size remains constant, this experience is a good parameter to understand the high stability of the colloid.

TEM studies

Transmission electron microscopy studies of cadmium colloids of varying concentrations were also carried out. These samples were prepared by dripping the colloidal solution on graphite-coated copper grids, allowing solvent to evaporate, and then TEM analysis is performed. Cd-ethanol colloid size ranges between 25–50 Å. The average size for Cd-2-propanol was found to be 50–75 Å (Table 1). The larger size of 2-propanol colloid is related with the lower stability at room temperature. The particles are spherical (see Fig. 1). Cd-2-methoxyethanol showed similar size to Cd-ethanol, being 30–50 Å average. However, Cd-2-butanone and Cd-DMSO exhibited similar particle size with 30 Å the smaller and 100 Å the larger particles (see Fig. 2). Since Cd-2-butanone showed larger particle size, it is less stable than Cd-DMSO. Also, it is important to consider the dielectric constant of the solvent. For comparison, CdS colloid was prepared and a larger size between 400–625 Å was obtained [24].

UV studies

Metal colloidal dispersions exhibited absorption bands in the UV and VIS regions of the spectrum. These are due to the plasma resonance excitation or interband transitions, which is an associated characteristic of metal nature of the particles [25].

Table 1 Particle size and stability of Cd colloids

Colloid[a]	Conc. × 10^2 [M]	Size [A]	Stability[b] (h)
Cd-ethanol[c]	1.71	25–50	2.5
	6.28	30–33	48
	3.17	20–42	48
	7.31	25–42	2 w
Cd-2-propanol	1.76	–	48
	1.73	42–50	4
	2.70	–	48
	1.55	50–63	2
	2.81	–	3
	3.70	50–75	2
Cd-2-butanone	2.69	63–100	6
	2.69	25–75	4
	2.15	33–100	4
	3.29	25–100	3
	4.04	25–100	3
Cd-DMSO[d]	1.96	100–133	48
	1.99	–	24
	4.36	33–75	2
	4.89	–	2
	1.73	25–50	2 w
	5.71	40–75	m
	5.48	–	m
Cd-2-MeEtOH	1.78	–	24
	1.78	–	25
	2.70	–	24
	2.62	25–50	1.5 w
	4.47	25–100	m
	2.47	30–50	m
	4.59	42–67	m
	6.62	–	m
Cd-DMF	1.78	67–267	2
	2.67	–	3
	2.65	50	3
	3.20	25–67	3
	4.89	–	1

[a] The colloids are negatively charged (ethanol and DMSO).
[b] Stability in h = hours, w = week, m = month.
[c] Zeta potential = + 1.14 V.
[d] Zeta potential = + 0.95 V.

A direct relation between stability and absorption bands for cadmium colloids was found. The most stable colloids (Cd-DMSO, Cd-2-methoxy ethanol, Cd-ethanol showed an absorption band at 285 nm. Some of the results are summarized in Table 2. A very relevant result is the UV spectra of Cd-2-methoxy ethanol after 1 month: the band at 285 nm was becoming sharper and the band's higher wavelength began to decrease (see Fig. 3A, B, C). This is probably due to the increase in particle size of the colloid from 50 to 150 Å. The polydispersity of the system is decreasing due to flocculation of the larger particles and the subsequent narrowing of the absorption bands.

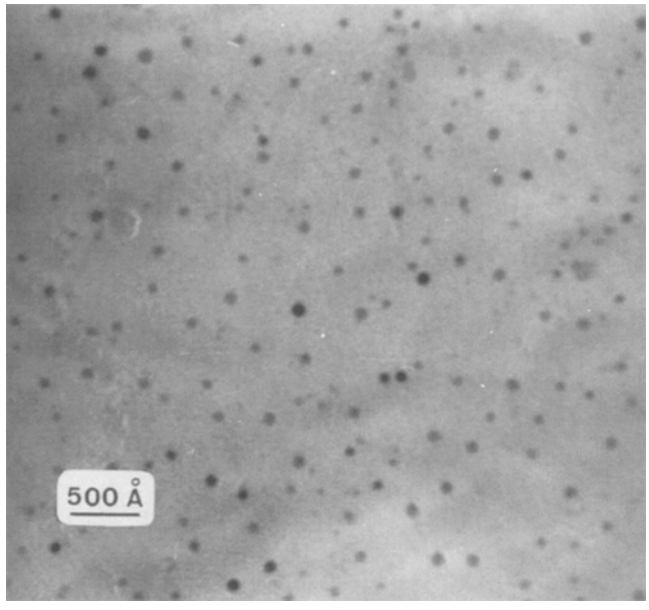

Fig. 1 TEM micrograph of Cd-2-methoxyethanol 4.59 × 10^{-2} M

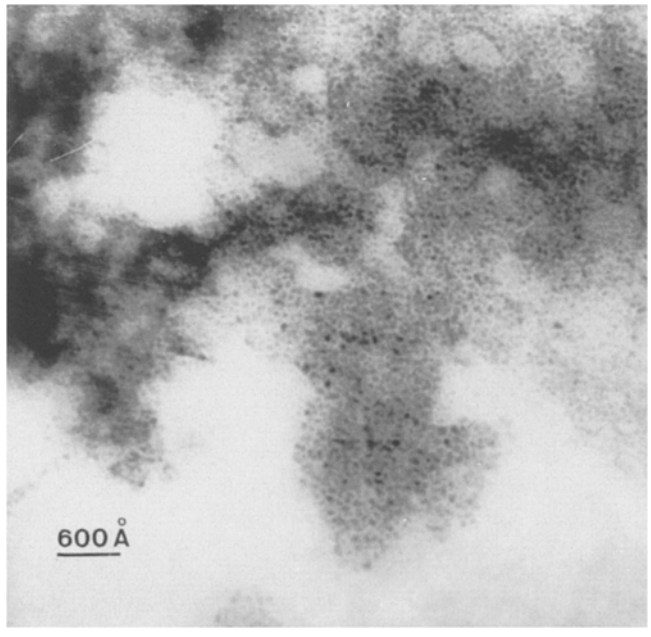

Fig. 2 TEM micrograph of Cd-DMSO 4.36 × 10^{-2} M

EDAX studies

The colloidal particles were also studied by EDAX in order to corroborate the Cd metal presence (see Fig. 4). In all the cases, Cd was observed.

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Table 2 UV absorption of Cd-colloids

Colloid	Conc. $[M] \times 10^2$	UV abs. (nm)
Cd-DMSO	4.36	284
	4.89	260
	1.23	259
Cd-ethanol	1.71	206; 248
	6.28	285
Cd-2-methoxyethanol	2.70	253; 303
	4.47	215; 294
	4.59	296
Cd-2-propanol	2.81	270; 278; 284
	3.70	275; 358; 312
Cd-DMF	3.20	265; 275; 350
	4.69	268
Cd-2-butanone	2.69	210; 298
	4.04	211; 303

Conclusions

We were able to obtain a very stable colloid of Cd-2-methoxy ethanol. No stabilizers of any kind were added, just the metal clusters dispersed in the solvent were used.

The metal colloids were mostly spherical and showed a size ranging from 25–130 Å.

From the UV data results, we can demonstrate that our results are according to theoretical calculations obtained from Craighton and Eadon [25], for spherical cadmium particles of 10 nm diameter in aqueous media. Also, these results are consistent with experimental values obtained by Henglein [26].

The colloids exhibited a spectrum depending upon the particle size, the larger particles absorbed at higher

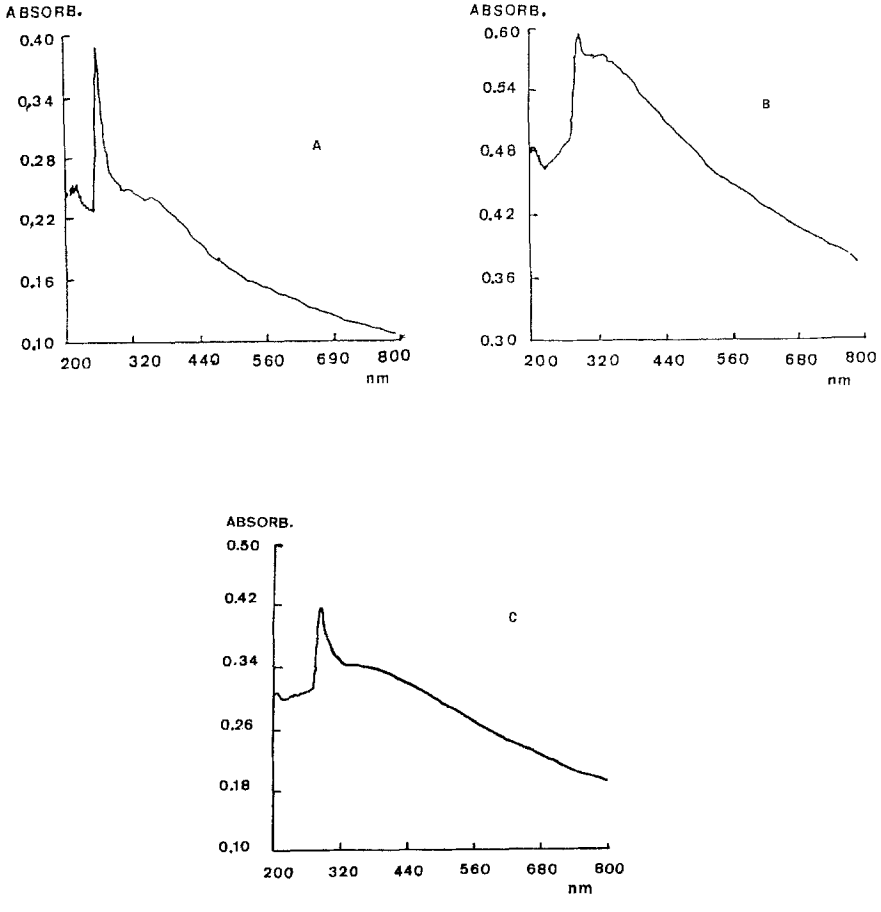
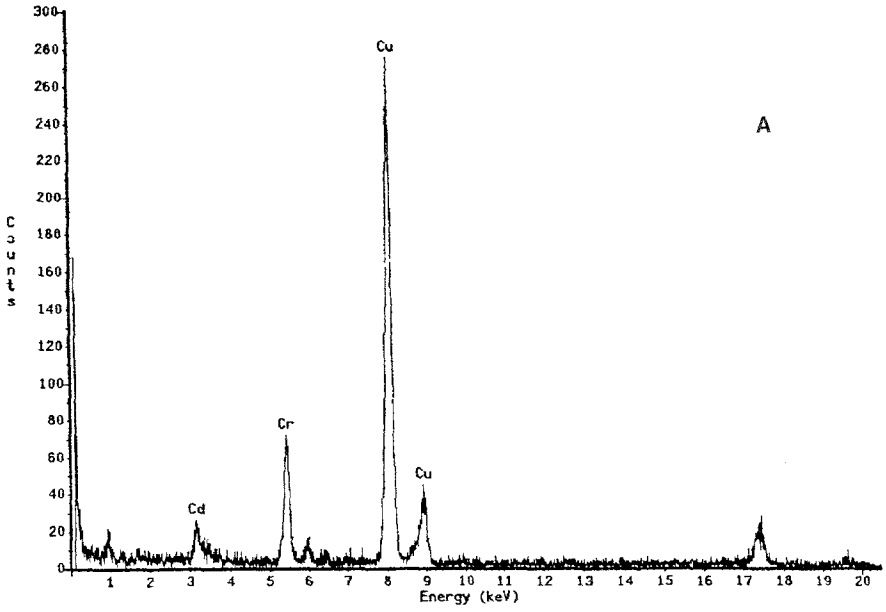


Fig. 3 **A** UV spectra of Cd-DMSO, **B** UV spectra of Cd-2-methoxyethanol colloids and **C** UV spectra of Cd-2-methoxy ethanol colloid after 35 days



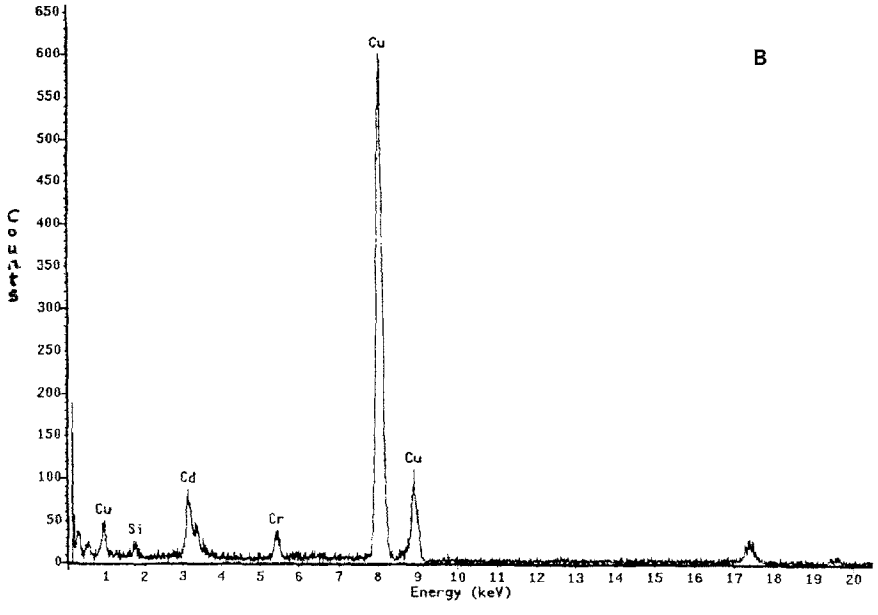


Fig. 4 *EDAX* of cadmium colloids **A** Cd-DMSO, **B** Cd-2-methoxyethanol

wavelength. Besides, there was a size range in which the absorption of the particles was not affected.

The colloids are resistant to the metal oxidation by oxygen gas bubbled directly on them. CdO formation was not observed.

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