Optical Properties of Platinum Particles Synthesized in Microemulsions

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We report the optical properties of nanosized ($\approx$4 nm) platinum particles synthesized in water-in-oil (w/o) microemulsions. The particles present a maximum at 220−256 nm, being highly position dependent upon the reaction medium. The aging of solutions causes cluster formation, whose absorption spectrum is rather different from those of the initial solutions with a second smaller maximum at longer wavelengths. In the extreme case when particles are separated from microemulsions and redispersed in water, a flat spectrum with a maximum at 260 nm appears. Changes in the optical absorption during reaction are used to propose a formation and stabilization mechanism of the particles. A comparison with the results of platinum particles obtained in water is also reported. Colloidal platinum was also obtained without hydrazine by heating. The optical properties of the metallic particles are identical with the properties of the corresponding particles prepared with hydrazine. This reaction is catalyzed by light. Various surfactants were used in order to propose a mechanism for the formation of the colloidal particles by this reaction pathway.

Introduction

Water-in-oil (w/o) microemulsions have been used for many years as microreactors for the synthesis of ultrafine metallic particles.[1−4] Since the pioneer works of Boutonnet et al.,[5] who studied the production of colloidal Pt, Pd, Rh, and Ir particles by hydrogen or hydrazine (N_2H_4) reduction in w/o microemulsions, many studies have been made on the synthesis of this type of material. On the other hand, only recently has there been developed an understanding of the optical properties of these colloids.[6,7] In the present study, colloidal Pt was synthesized by reducing H_2PtCl_6 with hydrazine in w/o microemulsions consisting of $C_{12}E_4$/*n*-heptane/water. It is shown that the optical properties of these particles can be related to the mechanism of their formation in these compartmentalized systems.

It is well-known that colloidal dispersions of metals exhibit absorption bands or broad regions of absorption in the ultraviolet−visible region. These are due to excitation of plasma resonances or interband transitions[6] and are thus a characteristic property of the metallic nature of the particles.[8−10] When particles are much smaller than the wavelength of light, the absorption coefficient (in $M^{-1} cm^{-1}$) can be obtained from the Mie theory using

$$\alpha = (18\pi V_m \cdot 10^4 n_0^3 \epsilon_2)/(\ln 10\lambda(\epsilon_1 + 2n_0^2) + \epsilon_2^2) \quad (1)$$

where V_m in $cm^3 mol^{-1}$ is the molar volume of the metal, ϵ_1 and ϵ_2 are the real and imaginary parts of the dielectric constant of the metal, and n_0 is the index of refraction of the solvent.

Calculations made by Creighton and Eadon[11] have predicted that there should be a peak in the absorbance spectra of colloidal Pt at about 215 nm in water, and Henglein et al.[4] have recently synthesized colloidal Pt showing this absorption peak. The Pt colloids we have obtained in microemulsions show a band in the absorption spectrum that is red-shifted with respect to the band position in water.

The objective of this work is the study of the optical spectrum of colloidal Pt prepared in microemulsions and to relate their

TABLE 1: Composition of the W/O Microemulsions for the First Series of Samples

sample	% (w/w) $C_{12}E_4$	% (w/w) H_2PtCl_6(aq)	[Pt(IV)]/M	R
P001	16.54	0.50	0.20	0.61
P002	16.54	1.01	0.20	1.20
P003	16.54	1.70	0.20	2.07
P004	16.54	2.47	0.20	3.01
P005	16.54	3.20	0.20	3.88
P006	16.54	4.06	0.20	4.96
P007	16.54	5.00	0.20	6.09

optical properties to the kinetics of the reaction carried out in their preparation.

Experimental Section

The preparation of the colloidal platinum particles was achieved by mixing two sets of w/o microemulsions, with H_2PtCl_6 in one set and N_2H_4 as the reducing agent in the other set. Excess of hydrazine (25% over the stoichiometric value) was added to ensure complete reduction of the platinum salt. All the experiments were carried out at room temperature under open air atmosphere. Several series of samples were prepared in order to study the influence of the preparation method on the optical properties of colloidal Pt particles. Six series with different salt concentrations were prepared (0.001−0.2 M). Droplet sizes were varied by changing the value of $R = [H_2O]/[C_{12}E_4]$ for each sample[12] ($R = 0.61−6.09$), and the salt concentration in the aqueous phase was kept constant for a particular series (Tables 1 and 2). Pt formation was confirmed by X-ray diffraction (XRD) and energy dispersive X-ray analysis (EDXA). We can conclude that single crystals are formed at room temperature from the agreement between the size determined by XRD ($D_{hkl} \sim 4.75$ nm) and transmission electron microscopy, TEM (D_{TEM}).

All the reagents were used as received without further purification. H_2PtCl_6 hydrate (99.995%), hydrazine monohydrate (98%), *n*-heptane (99%), and dioctyl sulfosuccinate sodium salt (AOT) (96%) were purchased from Aldrich, and tetraethylene glycol dodecyl ether, $C_{12}E_4$ (Brij 30), was from Fluka. Solutions were prepared with doubly distilled water.

TABLE 2: Several Series of Samples Differing Only in the [Pt(IV)] in the Aqueous Phase

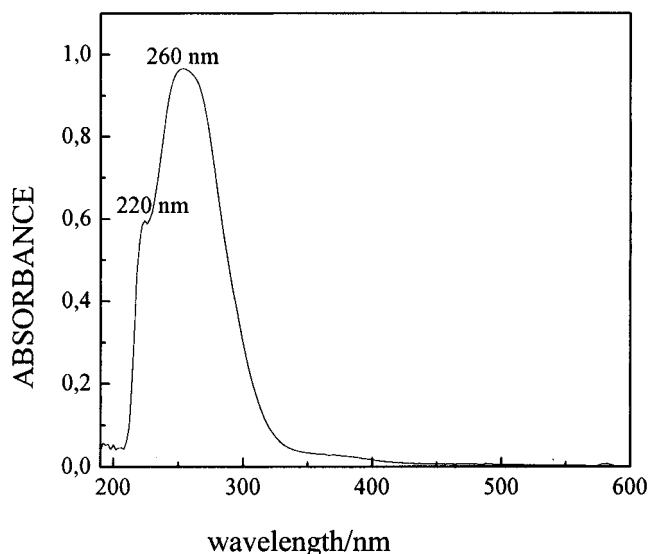|	2nd series P008−P014	3rd series P015−P021	4th series P022−P028	5th series P029−P035	6th series P036−P042
[H_2PtCl_6]/M	0.1	0.05	0.025	0.01	0.001

Figure 1. Absorption spectrum of H_2PtCl_6 in the $C_{12}E_4$/*n*-heptane/ water microemulsion and 0.01 M platinum salt concentration.

Absorption spectra of the colloids and kinetic measurements were recorded on a Hewlett-Packard HP8472 spectrophotometer in 1 cm light path length cuvettes.

For the transmission electron microscopy measurements, a drop of the colloidal solution was placed on a carbon-coated copper grid covered with an acetate cellulose polymer prepared and deposited just before the experiments. After evaporation of the solvent, micrographs were recorded on a transmission electron microscope (Philips CM12) working at 80 kV. For high-resolution micrographs a JEOL 2000 TEM microscope working at 200 kV and equipped with an EDXA detector was used.

Photon correlation spectroscopy (PCS) measurements were performed with an Ar laser Liconix Series 5000 of 5 W operating at $\lambda = 488$ nm and a goniometer ALV-SP80 controlled automatically by means of an ALV-LSE unit. The data were adjusted using the inverse Laplace transform (ILT) method.

Colloidal production without hydrazine was investigated by heating a microemulsion containing H_2PtCl_6 with and without light irradiation and keeping it at constant temperature in a thermostatic bath.

Results and Discussion

UV−vis Spectroscopy. In Figure 1 the absorption spectrum of H_2PtCl_6 in the microemulsion system is shown. As can be observed, there are two different bands, one centered at 220 nm and the other at 260 nm. When the microemulsion with the reducing agent is added to the microemulsion containing H_2PtCl_6, these bands disappear, and a new peak centered at 236 nm, the only peak in the absorption spectra, appears after a few minutes. In Figure 2 we show the absorbance evolution at 260 and 220 nm, as well as some sequences of the changes in the band shape with time. It can be seen (Figure 2a,b) that after 1000 s the absorbance at 264 nm becomes nearly zero, but not at 220 nm because this is also the wavelength of the plasmon absorption band of the Pt particles, which are still growing. At the latter wavelength (220 nm) the absorbance increases with time until 2220 s (Figure 2c) and then decreases again while a new band appears at 236 nm (Figure 2d,e). These results can

be explained by assuming that two different steps are involved during the formation and stabilization of the particles. In the first step, the particles are formed inside the aqueous droplets, and the absorption band (220 nm) lies very near to the theoretical band position in water (215 nm).[11] In the second step, some kind of interaction between the particles and the microemulsion (chemisorption or physisorption of the surfactant molecules) causes the displacement of the observed band to 236 nm. This eventual sorption of surfactant molecules is responsible for the excellent particle size control which can be achieved using microemulsions.

We have also reduced H_2PtCl_6 in water with hydrazine in the presence of $C_{12}E_4$ in order to avoid flocculation. In this case, the predicted maximum at about 215 nm is not observed, and only a great increase in the absorption coefficient below 300 nm is evident (Figure 3). Henglein et al.[4] have also recently observed that, in Pt colloids synthesized in water by the citrate method, the band predicted by Creighton and Eadon does not appear, which agrees with our experimental results. Differences in the surface dielectric constant of the particles, arising from different methods of synthesis, are responsible of this particular behavior. Henglein et al.[4] have calculated the spectra from two sets of dielectric constants (taken from refs 13 and 14) and obtained completely different results.

The band that appears in the optical spectra of Pt in microemulsion, when the salt reduction has been completed, is caused by the electronic surface excitation due to the electric field of the incoming light (taking into account that chloride anions that are formed in the reduction of $PtCl_6^{2-}$ absorb below 220 nm). From eq 1 it can be concluded that a plasmon band is located at the wavelength where the condition $\epsilon_1 = -2n_0^2$ is fulfilled. For Pt, this should occur at about 300 nm.[14] However, as ϵ_2 is large and ϵ_1 strongly changes with wavelength, it is expected that the plasmon absorption is weak and the band shifts to lower wavelengths. In our experiments the reaction media strongly influences both the position and width of the plasmon band (see Figures 4 and 5). Wilcoxon et al.[10] have also observed this influence of synthesis variable in the optical properties of colloidal gold (with band displacements of more than 15 nm). This sensitivity of the plasmon band of particles with the surface properties is very characteristic of small metallic particles.[15,16]

The wavelength at which a maximum absorption occurs can be calculated from the Mie theory according to the equation

$$\lambda_m^2 = \lambda_c^2(\epsilon_0 + 2n_0^2) \tag{2}$$

$$\lambda_c^2 = (2\pi c)^2 m/4\pi N_e e^2 \tag{3}$$

where λ_m is the wavelength at the maximum, ϵ_0 is the high-frequency contribution to the dielectric constant of Pt, and λ_c is the plasma wavelength of the bulk metal in terms of the effective electron mass, m, and the electron density, N_e (cm^{-3}). The plasma wavelength varies inversely with the square root of the free electron concentration. Therefore, the adsorption of molecules increases the electron density (by electron donation or possibly by the squeezing of the free electrons of the metal into a smaller volume of the particle), resulting in a blue-shift of the band position. Adsorbed anions can then change both the plasma absorption intensity and spectrum. This fact is apparently due to changes in the dielectric constant of the surface layer around the particles, with the result that the resonance condition for plasmon absorption is no longer fulfilled.[7,12]

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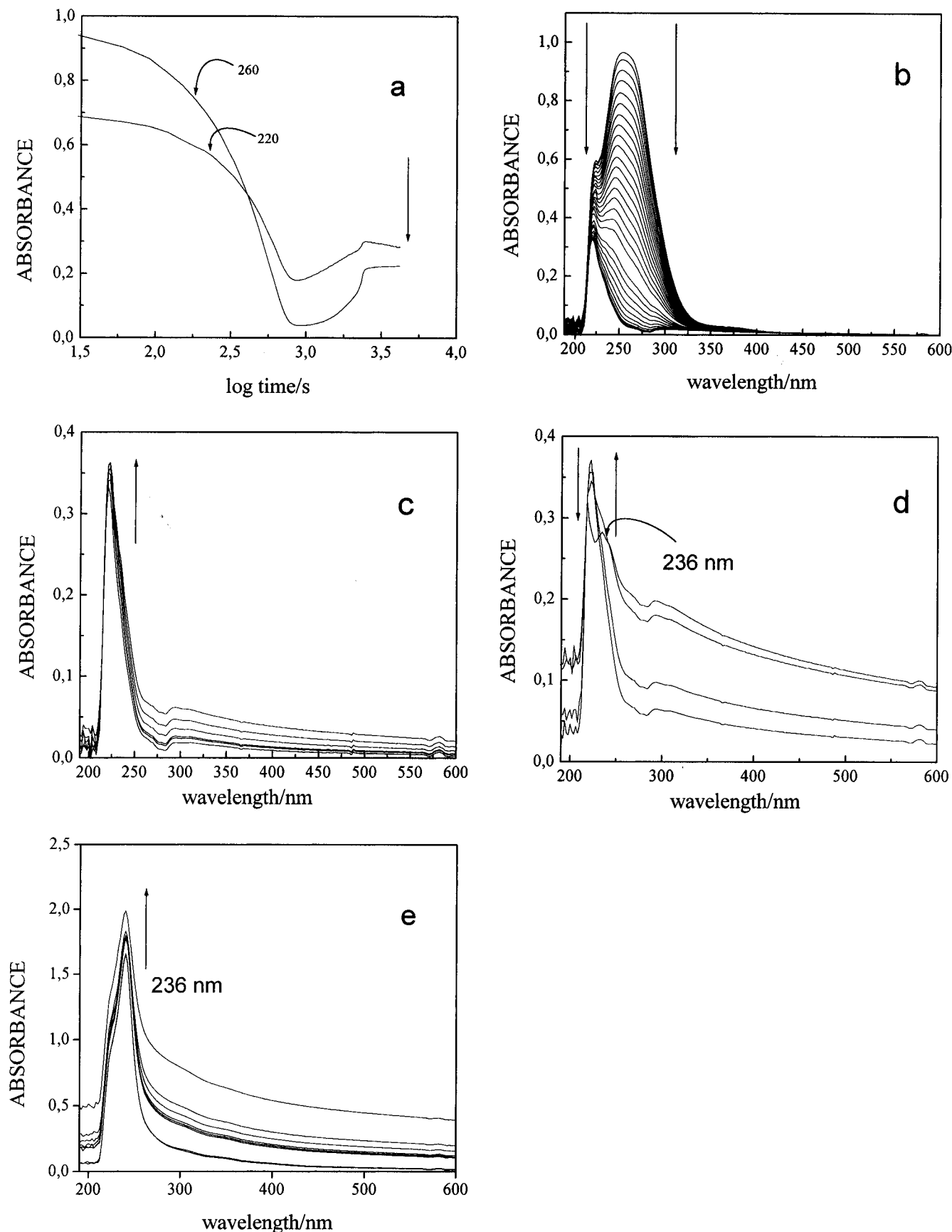

Figure 2. (a) Evolution of the absorbance at 260 and 220 nm during reaction. (b) When the microemulsion containing hydrazine is added to the microemulsion with platinum salt, the characteristic bands for the salt disappear and (c) after some seconds the characteristic absorption band for Pt particles in water (220 nm) starts to grow. (d) After that the absorbance at 220 nm decreases while a new peak at 236 nm appears. (e) This is the only peak in the spectrum when reaction has completely finalized, and no further changes were observed after several weeks. In these experiments the concentration of platinum salt was 0.005 M.

It was observed that in the case of colloids P036−P042, where [Pt(IV)] inside the droplets is at least 10 times lower than in

the other series of samples, the band is red-shifted, which can be associated to a minor degree of chloride ion adsorption
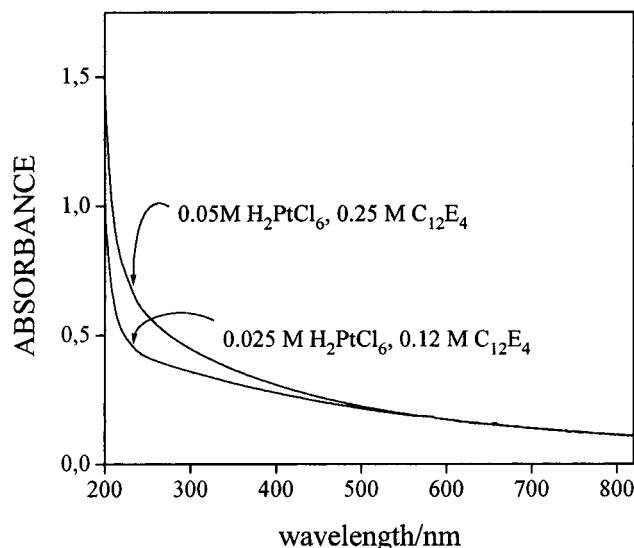
Figure 3. Absorption spectrum of colloidal Pt synthesized in water with hydrazine and $C_{12}E_4$. The upper line is 0.05 M H_2PtCl_6, 0.25 M $C_{12}E_4$, and the bottom is 0.025 M H_2PtCl_6, 0.12 M $C_{12}E_4$. Excess of hydrazine was used (25%). Resonance condition for plasma oscillation is not fulfilled.

because decreasing amounts of these ions are formed when lower concentrations of $PtCl_6^{2-}$ ions are reduced. This red-shift can be observed in Figure 4a. As confirmation, Cl^- ions in the form of NaCl were added to the microemulsion P042, in which the maximum of the absorbance lies at 256 nm. A displacement to 252 nm and a band damping was observed (Figure 4b).

In the series P036—P042, the sequence of maximum absorption for the samples characterized by $R = [H_2O]/[C_{12}E_4]$ values in the range 0.61—6.09 exhibits a red-shift from 246 to 256 nm (Figure 5). Extensive work has been carried out by high-resolution transmission electron microscopy (HR-TEM) in order to determine the size of the particles in that series, and the results show that the particle size is very small ($\approx$3.5 nm) and of narrow size distribution (Figure 6). Because the variation in mean particle size is small over this series, we believe that the dielectric overlayer coating thickness of the particle (if we assume that the overlayer thickness decreases with particle radius)[12] is approximately the same for all the samples. If so, it cannot be responsible for the band displacement. A possible explanation of this effect can be that as droplet size grows conditions for surfactant adsorption over the particle surface are more favorable. Surfactant adsorption has been described as proceeding through a series of stages in which the surfactant film has to adopt high positives curvatures.[15] By increasing the droplet radius, we are favoring positive (or less negative) curvatures[16] and therefore enhancing the adsorption of surfactant. In Figure 7a we show this possible mechanism of stabilization for the particles. Pileni et al.[15] proposed the possibility of small aggregate formation surrounding the particle. (Hence, two micellar populations could be in equilibrium.) A different mechanism of stabilization is probably more appropriate for explaining the behavior of the smallest droplets ($R = 0.61$). For this case, the particle size and the droplet size are very similar (as we have determined by PCS measurements, the hydrodynamic radius for $R = 0.61$ is about 3.5 nm), and an "implosion" of the droplet over the particle surface activated by a collision with an empty droplet may occur, giving rise to a higher degree of surfactant adsorption than in the other cases (Figure 7b). This could be the reason for the λ_{max} observed for these experiments (Figure 5, inset) being higher than for others with values of $R = 2$ or even more.
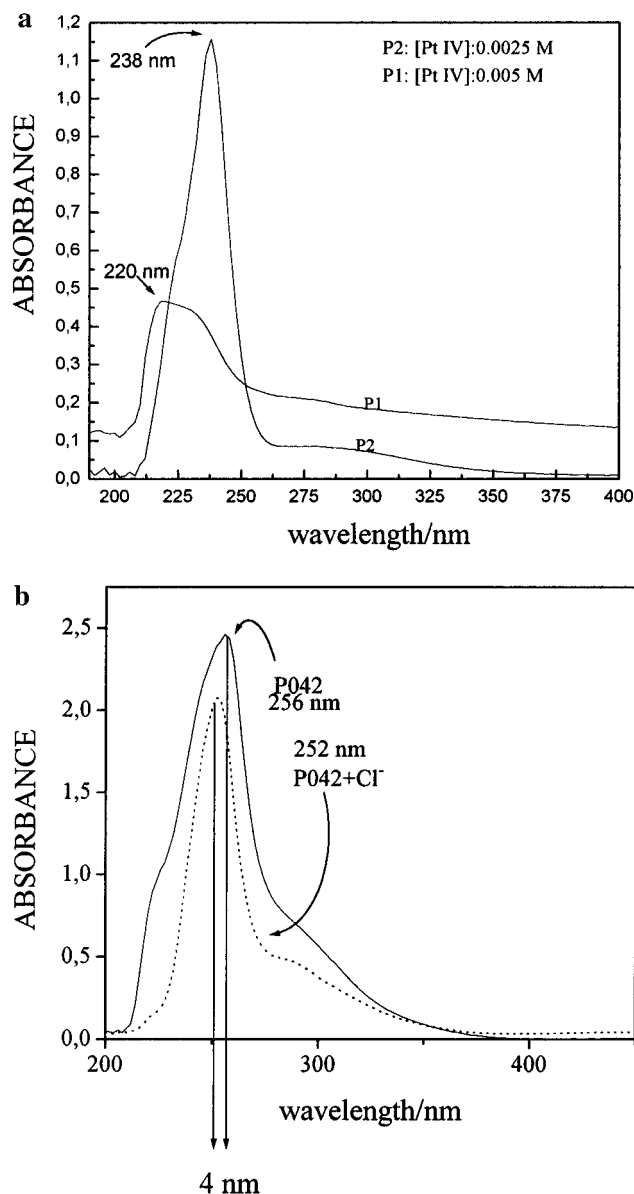

Figure 4. (a) Influence of the H_2PtCl_6 concentration on the plasmon band position. (b) Blue-shift observed by adding NaCl to the microemulsion P042.
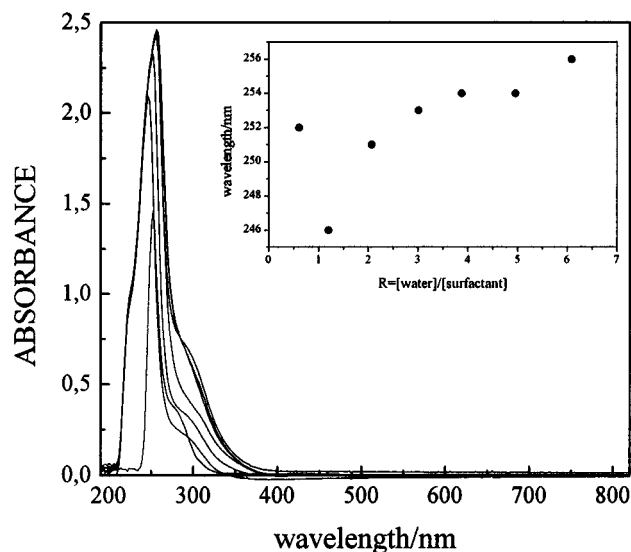

Figure 5. Absorption spectra for samples P036—P042. The droplet size, characterized by $R = [water]/[surfactant]$, is the only difference. Red-shifting of the maximum with droplet size (inset) is shown. In the first point, $R = 0.42$; droplet and particle size are very similar, and adsorption is more favorable.
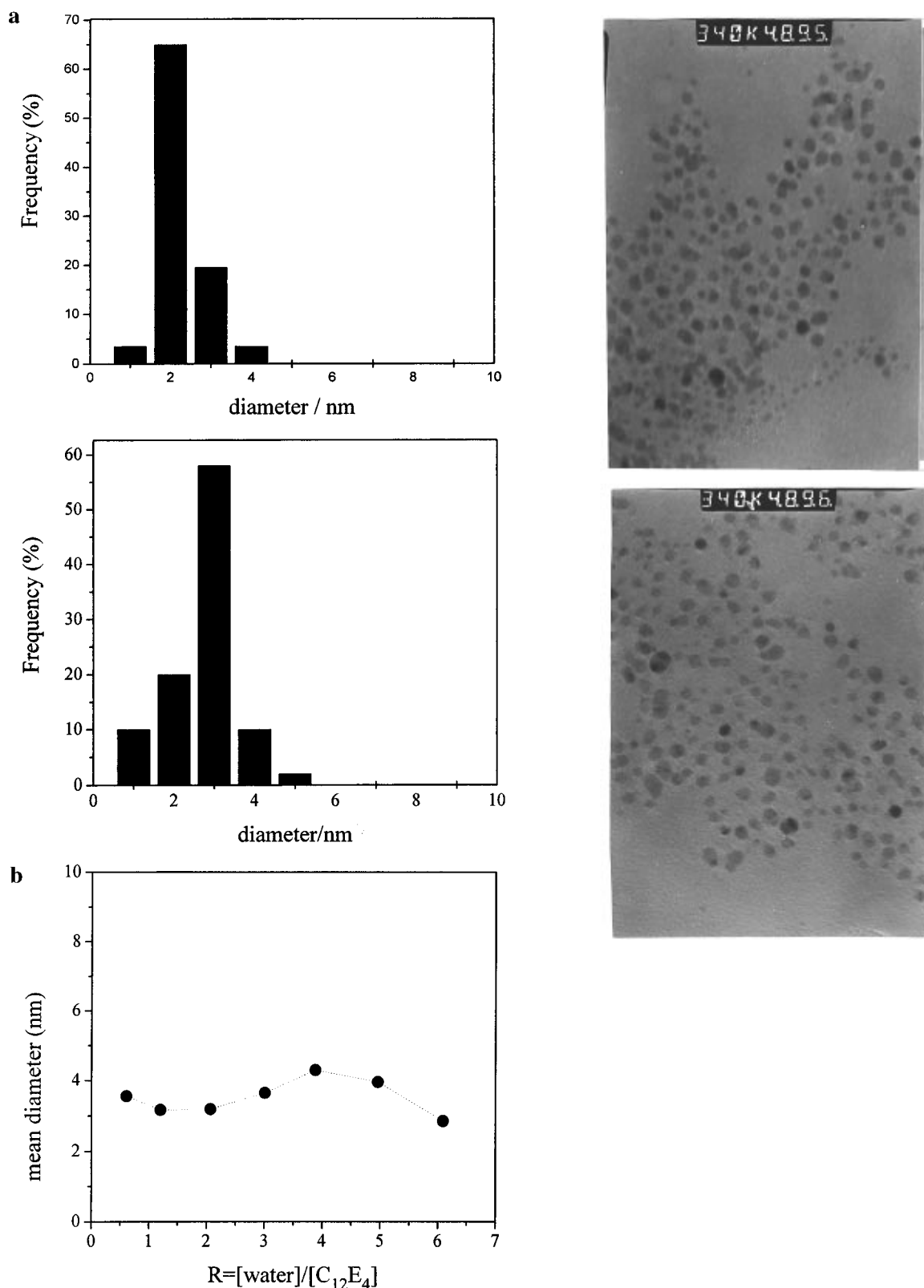
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Figure 6. Typical TEM size distribution showing the narrowing of size dispersions and evolution of mean particle diameter with droplet size for the samples P036−P042. The scale for both TEM pictures is 1 cm = 32.3 nm.

To corroborate these hypothesis, we have carried out PCS experiments on the microemulsions before and after reduction of the platinum salt. All the measurements were made at 25 °C and at different scattering angles (60°, 90°, 120°). If the particle is surrounded by a coat of surfactant, the volume of the water pool remains constant, whereas the interfacial area of the empty droplets decreases. Hence, the water pool radius of an empty droplet is expected to increase.[15] In Figure 8 the results for a $C_{12}E_4$/n-heptane/$H_2PtCl_6^{2-}$(aq) microemulsion with

$R = 1$, $[H_2PtCl_6^{2-}] = 0.1$ M, and $\Phi = 0.05$ (Φ = volume fraction of droplets) are presented. Before the reduction only the narrow peak corresponding to microemulsion droplets appears (3.3 ± 0.3 nm). About 36 h after the reduction, two peaks, one at 1.7 ± 0.2 nm and a broader at 4.5 ± 0.5 nm, become visible. As expected, a small increase in the droplet radius or in the width of the droplet size distribution occurs. The other peak at 1.7 nm arises from the particles formed, as the TEM study has evidenced (see also Figure 6).
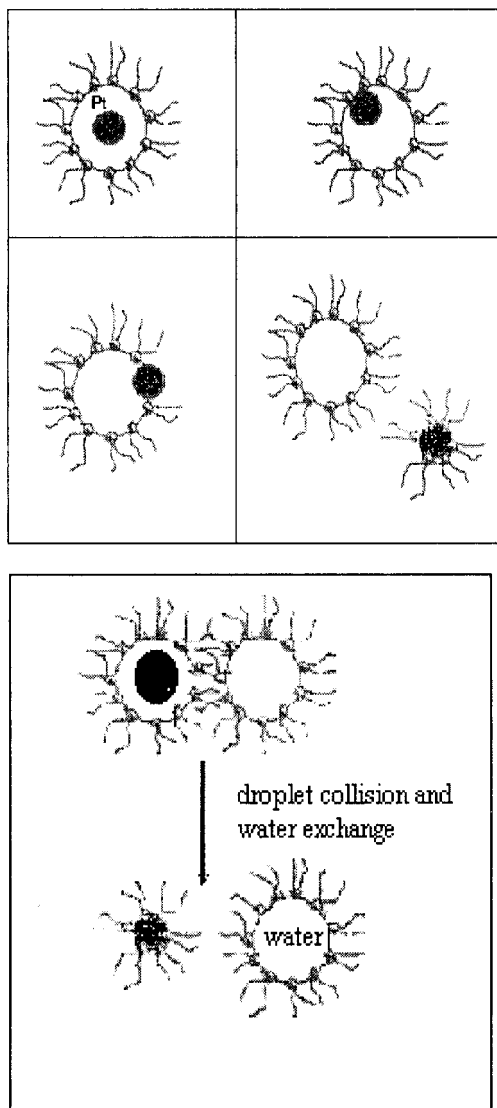
Figure 7. Model of particle stabilization by the surfactant molecules. Adsorption on the particle surface occurs with changes in the local curvature of the film for the larger R ("Pileni's mechanism) (a, top). When R is very small (b, bottom), the particle size and the droplet size are very similar, and a different mechanism activated by droplet collision is proposed ("implosion mechanism").

Aging Effect. We have also studied the solutions aging in order to check the influence of agglomeration on the absorption spectrum of platinum. The agglomeration of particles may occur upon the aging of solutions that initially contain isolated particles, producing a great change in the absorption spectrum. This has been observed for suspensions of cadmiun and thallium[17,18] particles. (It should be noted that for these metals a second maximum appears at higher wavelengths.) Even very small amounts of colloid association can alter the UV−vis absorbance.[19] A broad maximum at 302 nm appears several weeks after sample preparation for colloidal Pt reduced in microemulsions which can be assigned to an agglomeration process (Figure 9). Particles centrifuged and washed with water several times were redispersed in water and in mixtures of C_2H_5-OH/water to adjust the band position according to eq 2. The 300 nm band is replaced by small and broad maximum at 260 nm (Figure 10). This is consistent with the formation of clusters of particles, because when particles form clusters the absorption spectrum becomes flatter and broader and the maximum appears at higher wavelengths than with of isolated particles. This effect is due to the dipole−dipole interaction of the agglomerated particles.[20] The cluster formation was confirmed by TEM both
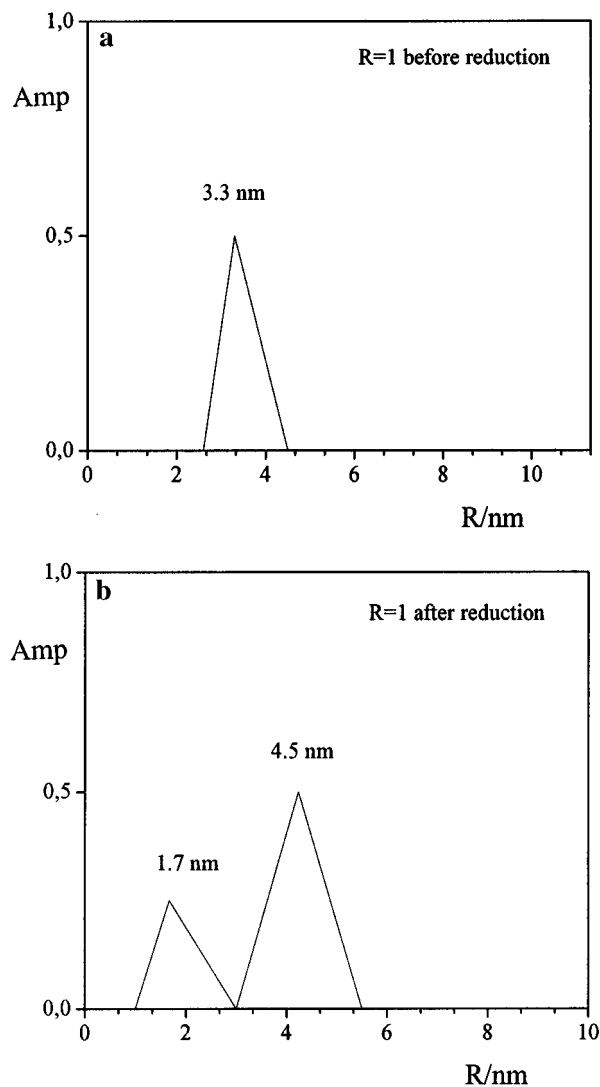

Figure 8. Photon correlation spectroscopic experiments reveal a small increase of the droplet size after the reduction (b) which suggest a stabilization mechanism of the particles by the surface coating with the surfactant molecules. The initial platinum salt concentration in these cases corresponds to the samples series P008−P014.
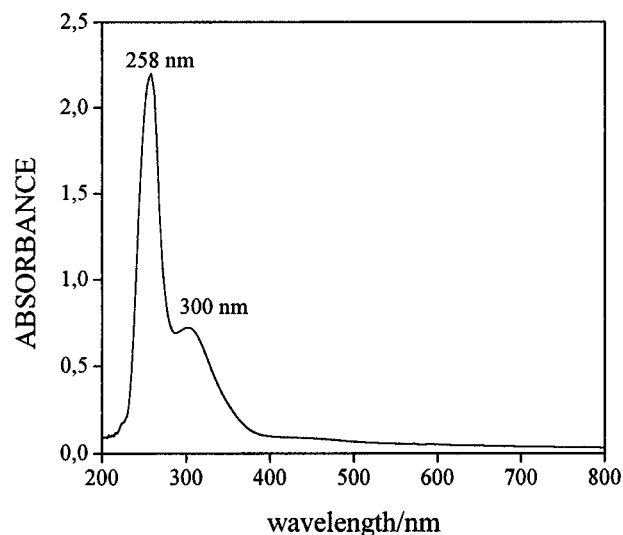

Figure 9. Absorption spectum of colloidal Pt after aging the solutions for several weeks. The initial platinum salt concentration corresponds to the samples series P008−P014.

in microemulsion and after washing the particles (Figure 10, inset). It is interesting to note that Robinson et al.[21] prepared

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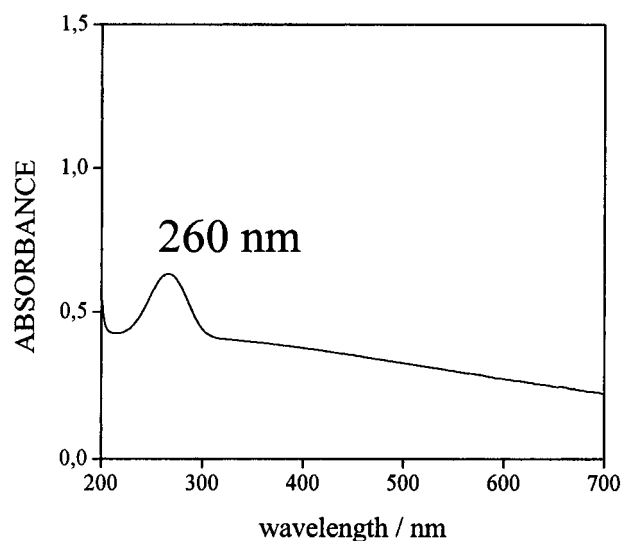*J. Phys. Chem. B, Vol. 101, No. 44, 1997* **9003**

Figure 10. Absorption spectrum of Pt particles (centrifuged and washed several times to separate from microemulsions) redispersed in water. In the inset a TEM micrograph confirms the cluster formation. We used the samples P008−P014. The scale for TEM picture is 1 cm = 40.0 nm.
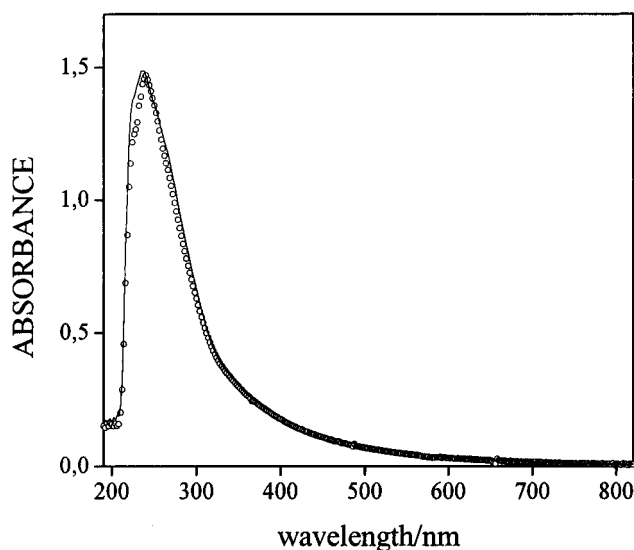

Figure 11. Comparison between optical properties of colloidal Pt chemically (line) and photochemically (circles) obtained. We have used an 0.01 M aqueous solution of platinum salt in both cases.
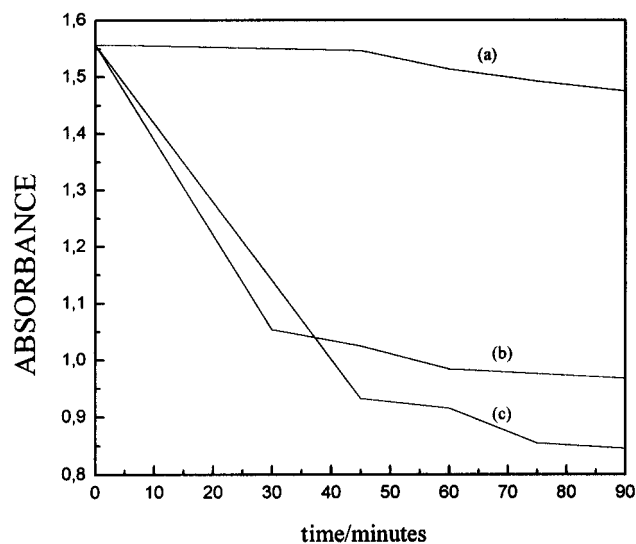

Figure 12. Reduction without hydrazine. Absorbance of platinum salt at 254 nm vs time. (a) at room temperature under laboratory light; (b) at 50 °C under laboratory light; (c) at 50 °C in the dark. The experiments have been carried out with 0.01 M initial platinum salt concentration.

platinum sols in glycerol/AOT/n-heptane microemulsions which showed an increase of the absorbance as the wavelength becomes smaller and a pronounced absorption shoulder at 460 nm. They suggested the possibility of formation of very small Pt clusters with different electronic properties from those of larger particles in order to explain this shoulder. A quantitative relationship between λ_{max} and size is not known, but qualitatively, for spherical colloids, many recent works suggest[22] that λ_{max} is blue-shifted to smaller wavelengths with decreasing particle diameter. Taking into account our results, both in water and in microemulsion, it seems more plausible to attribute the presence of this maximum to the presence of agglomerated particles.

Colloidal Production without Hydrazine. The formation of platinum colloids in w/o microemulsions without the addition of reductant was studied. Nowadays, the nature of the reducing agent in the so-called "photochemical colloidal" production is not completely understood, and several hypothesis have been formulated.[23] Microemulsions containing only the platinum salt were exposed to daylight for several days, and only after more than one month small changes in the spectra were measurable. But when microemulsions are exposed to daylight and kept at the same time in a thermostatic bath at ∼50 °C, the process is

strongly accelerated, and a typical brown color appears after only few minutes. The optical spectra of the generated colloids are identical with those obtained by hydrazine reduction (Figure 11). It should be mentioned that Barnickel et al.[12] have also synthesized Ag colloids in $C_{12}E_5$/cyclohexane/water microemulsions only using daylight irradiation of the $AgNO_3$ dissolved in this system. They explained their results, assuming that the terminal hydroxyl groups of the $C_{12}E_5$ surfactant, which are oriented toward the inner part of the droplets, are capable of reducing Ag^+ ions upon irradiation. To check their hypothesis, we have tried to obtain Pt by keeping samples at different temperatures with/without exposure to light irradiation but changing the system to AOT/n-heptane/water, because in this surfactant there are no terminal hydroxyl groups. Figure 12 shows the evolution of the absorbance at 254 nm under different experimental conditions. Very small changes can be observed at room temperature. At 50 °C the reaction produces a typical brown color which appears after few minutes. It can also be observed that the reactions are catalyzed by exposure to daylight, but the reaction is strongly dependent on the temperature due to the chemical reduction by the surfactant molecules. After 48 h at 50 °C the microemulsion shows a spectrum identical

with that observed by Pt particles obtained by hydrazine reduction, confirming the formation of colloidal Pt particles without reductant addition. As the heads of the ionic surfactant AOT are composed of sulfonate groups, the reduction can be explained by assuming that the electronic pairs of the oxygens in the sulfonate group donate the electrons, causing reduction during irradiation, such as the oxygens of the hydroxyl groups of the $C_{12}E_5$ molecules.

It can then be concluded from these results that electronic pairs of the oxygen are directly implicated in the reduction process, and if this is true, any other molecules with atoms or groups of atoms capable of electron donation could be effective in the production of silver and platinum (or other particles of noble metals). This has been confirmed by observing the formation of platinum particles in water by just adding sodium methyl sulfate.

Conclusions

The present results show that platinum particles obtained in microemulsions present an absorption band at ∼220 nm which can be red-shifted depending on the reaction medium. The variations in the optical properties as the reaction progresses can be related to the mechanism of formation and stabilization of the particles.

The aging of solutions causes changes in the optical properties due to the aggregation clustering of particles, which was observed several weeks after particles were synthesized in microemulsions.

Colloidal Pt were produced by heating the microemulsion without adding any chemical reducing agent. It was observed that light is not responsible for this "unusual" reaction for colloidal production and that it behaves only as a catalyzer. Finally, a possible mechanism based on the electron donation by the electron pairs of the oxygens is proposed.

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