

# Formation of Thin Films of Platinum, Palladium, and Mixed Platinum:Palladium Nanocrystallites by the Langmuir Monolayer Technique

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Chloroform solutions of colloidal platinum, palladium, and mixed platinum:palladium = 1:1 particles were prepared by using a solvent extraction technique with distearyldimethylammonium chloride surfactant. The metal colloid solutions were dispersed on a water subphase in a Langmuir trough to generate particulate films and their surface pressure vs surface area isotherms were determined. The structures of the films were investigated by using Brewster-angle microscopy and transmission electron microscopy. It was demonstrated, by in situ reflectivity measurements, that the films had thicknesses in the order of 30 Å. Transfer of the films to solid substrates was investigated by using standard Langmuir-Blodgett techniques.

## Introduction

Precious metal particles have been extensively studied in terms of their internal structure and growth mechanisms<sup>1</sup> and because of their valuable physical properties, which have been exploited (particularly in the field of catalysis).<sup>2</sup> The work reported here describes the preparation of particulate films of nanosized platinum, palladium, and mixed platinum:palladium = 1:1 colloids. It has recently been demonstrated in our laboratories that suitable solutions of surfactant-stabilized particles of materials such as CdS,<sup>3</sup> Ag,<sup>4</sup> Fe<sub>3</sub>O<sub>4</sub>,<sup>5</sup> and TiO<sub>2</sub><sup>6</sup> can be dispersed on aqueous subphases in a Langmuir film balance and subsequently compressed to generate monoparticulate films of controlled interparticle separation. Particulate films of trioctylphosphine oxide-stabilized CdSe nanoparticles have also been prepared by using similar methodologies.<sup>7</sup> These films have been successfully transferred to solid substrates, and the subsequent formation of a range of layered devices is currently under investigation. The formation of particulate films of Pt, Pd, and mixed Pt:Pd = 1:1, as described in the present report, thus extends the range of useful systems that may be created.

Although generally prepared in aqueous solution, colloidal dispersions of metal particles may also be produced in organic solvents by a number of techniques, such as gas evaporation,<sup>8</sup> solvent extraction/reduction,<sup>9-11</sup> decomposition of an organometallic precursor,<sup>12</sup> and

phase transfer of preprepared particles from an aqueous to organic phase.<sup>13,14</sup> The colloidal metal solutions used here to form particulate films were prepared by the solvent-extraction technique, since it is applicable to a wide range of metal salts and typically produces particles with small diameters and narrow size distributions. The particulate films were investigated by a range of physical techniques, including Brewster-angle microscopy (BAM), transmission electron microscopy (TEM), and reflectivity.

## Methodology

Pt, Pd, and mixed Pt:Pd = 1:1 colloids were prepared by the extraction of aqueous metal salts into chloroform with distearyldimethylammonium chloride (DDAC) surfactant, by using established methodologies.<sup>9-11</sup>

**Platinum.** DDAC (20 mL, 1.0-mM) in chloroform was combined with H<sub>2</sub>PtCl<sub>6</sub> (20 mL of 0.5 mM) in triply distilled water, and the mixture was stirred for 12 h. The platinum-containing chloroform solution was separated by using a separating funnel and was transferred to a three-necked flask. The solution was then brought to reflux at 80 °C under argon flow and reduced by the addition of 1 mL of 0.01 M formaldehyde and 1 mL of 2 M sodium hydroxide. Reflux was continued for 2 h, after which time a clear, dark brown solution had been produced.

**Palladium.** Extraction of PdCl<sub>2</sub> by DDAC into chloroform was achieved by using a similar protocol. Twenty milliliter quantities of 0.5 mM PdCl<sub>2</sub> in water and 1.0 mM DDAC in chloroform were mixed for 12-h prior to separation of the organic fraction. Reduction was then carried out at room temperature through the addition of a 3-fold excess of sodium borohydride to the

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palladium/chloroform solution with stirring. The solution became dark brown in color.

**Platinum/Palladium.** Mixed platinum:palladium particles of 1:1 molar ratio were produced by the combination of equal volumes of the chloroform solutions of extracted Pt and Pd salts, prepared as described above. The metal ions were then reduced via the addition of a 3-fold excess of sodium borohydride under stirring, at room temperature, and a brown-colored solution was produced.

Surface pressure ( $\Pi$ ) vs surface area ( $A$ ) isotherms were determined for the three types of metal colloid/DDAC/chloroform solutions and for a DDAC/chloroform solution by spreading the appropriate quantities of the material dropwise onto distilled water in a Lauda film balance. Evaporation of the carrier solvent was permitted for about 20 min prior to measurement of the isotherms. Compression and expansion were carried out at very slow rates (0.05–0.1 cm/s). At higher surface pressures and compression rates (over 0.3 cm/s), spillage of the film over the trough edges occurred, which was attributed to the high viscosity of these films. Consequently, all isotherms were obtained by using very slow compression rates (0.05–0.1 cm/s).

The films were examined on the millimeter scale by BAM, performed in a homemade Teflon trough, and by using illumination from an Ion Laser Technology, 750-mW argon ion laser. Further details about the experimental setup have been given previously.<sup>15</sup> The structure of the particulate films was investigated at high magnification by using TEM. Samples were supported on carbon-coated, Formvar-covered, copper TEM grids and examined at 200 kV by using a JEOL 2000FX electron microscope. Transfer of the particulate films to sample grids was attempted by passing a grid vertically through the air–solution interface and picking up the film horizontally from the solution. Very poor transfer was achieved at low surface pressures, probably due to distortion of the film structure upon insertion of the grid through the film. Therefore, data were only recorded for films at high compressions.

The thicknesses of the films were estimated in situ on the water subphase by using reflectivity measurements. The intensity of light reflected from compressed films at surface concentrations of approximately  $50 \text{ \AA}^2$ /unit which were prepared in a Langmuir trough was measured as a function of the incident angle. Similar reflectivity measurements were performed on the pure water subphase, and the resulting curves were fitted by SigmaPlot 5.0 software by using a model based on the Fresnel equations.<sup>16,17</sup>

Langmuir–Blodgett (LB) films were prepared by compression of the particulate film to a surface pressure of 15–30 mN/m and maintenance of the film at constant pressure. The films were transferred to solid substrates of either glass or silanized glass by using a slow dipping rate of 0.1 cm/s and residence times of 30 s and 4.5 min in the solution and air, respectively. More rapid dipping rates resulted in poor transfer of the films (both pure surfactant and particulate) due to their high viscosities.<sup>18</sup>

## Results and Discussion

Dispersion of the metal particle solutions on water resulted in the production of uniform films which were visible only at higher compressions due to a very pale gray/brown coloration. The  $\Pi$  vs  $A$  isotherms which were obtained from the DDAC surfactant-coated Pd (Pd/DDAC), Pt (Pt/DDAC), and mixed Pt:Pd = 1:1 (Pt:Pd/DDAC) particulate films are shown in Figure 1a–c, respectively, and are compared with the isotherms from pure DDAC monolayers (Figure 1d). The area per unit is given on all isotherms, with respect to the concentration of DDAC molecules only, and does not consider the metal particles present. The isotherm corresponding to DDAC alone shows a simple S form, comprising the onset of a pressure increase at a surface concentration of approximately  $160 \text{ \AA}^2$ /unit and collapse at  $45 \text{ \AA}^2$ /unit and surface pressure of 46 mN/m. In contrast, all of the metal particle/DDAC isotherms show more complicated behavior, displaying a plateau region at surface pressures of about 45 mN/m, the value at which a pure DDAC monolayer collapses. The  $\Pi$  vs  $A$  isotherms generated from the colloidal metal/surfactant solutions were highly reproducible and were entirely reversible up to surface pressures of about 40 mN/m. Reversibility was lost upon compression to pressures in the order of 60 mN/m, as was evidenced by a shift in the isotherms to smaller surface concentrations; this may result from permanent structural changes in the particulate film and from some loss of material during compression.

It is useful to compare the  $\Pi$  vs  $A$  isotherms of DDAC-coated Pt, Pd, and Pt/Pd particulate films with the nanosized CdS/dodecylbenzenesulfonic acid,<sup>3</sup> and Ag/oleic acid<sup>4</sup> investigated previously. The plateau region in the  $\Pi$  vs  $A$  isotherm for the CdS/dodecylbenzenesulfonic acid films was interpreted in terms of a phase transition from monoparticulate crystalline agglomerates to a film of approximately three-particle thickness; dodecylbenzenesulfonic acid did not, on its own, form a contiguous monolayer at the air/water interface. In the spreading of oleic acid coated silver particles, the plateau region occurred at a surface pressure which was identical to the collapse of pure oleic acid monolayers.<sup>4</sup> This was attributed to extrusion of the oleic acid molecules, yielding a film which was formed from the surfactant-coated, silver-particle domains only. The Pt: Pd/DDAC system is somewhat different. The DDAC surfactant forms good monolayers, in the absence of additional colloidal particles, which also collapse at surface pressures corresponding to the plateau regime of the mixed-metal particle/surfactant isotherms (see Figure 1d). However, it seems likely that the Pt: Pd/DDAC films contain domains of surfactant-coated metal particles and surfactants in a purely organic environment. Collapse of the surfactant domains began at the onset of region II. Extrusion of DDAC from the film then occurred throughout region II and continued during region III. In an ideal surfactant system, extrusion of the component of lower collapse pressure would be complete at the end of the plateau region.<sup>19</sup> However, the binding of DDAC molecules to the metal core of the particles, or even to the outer organic shell, is expected

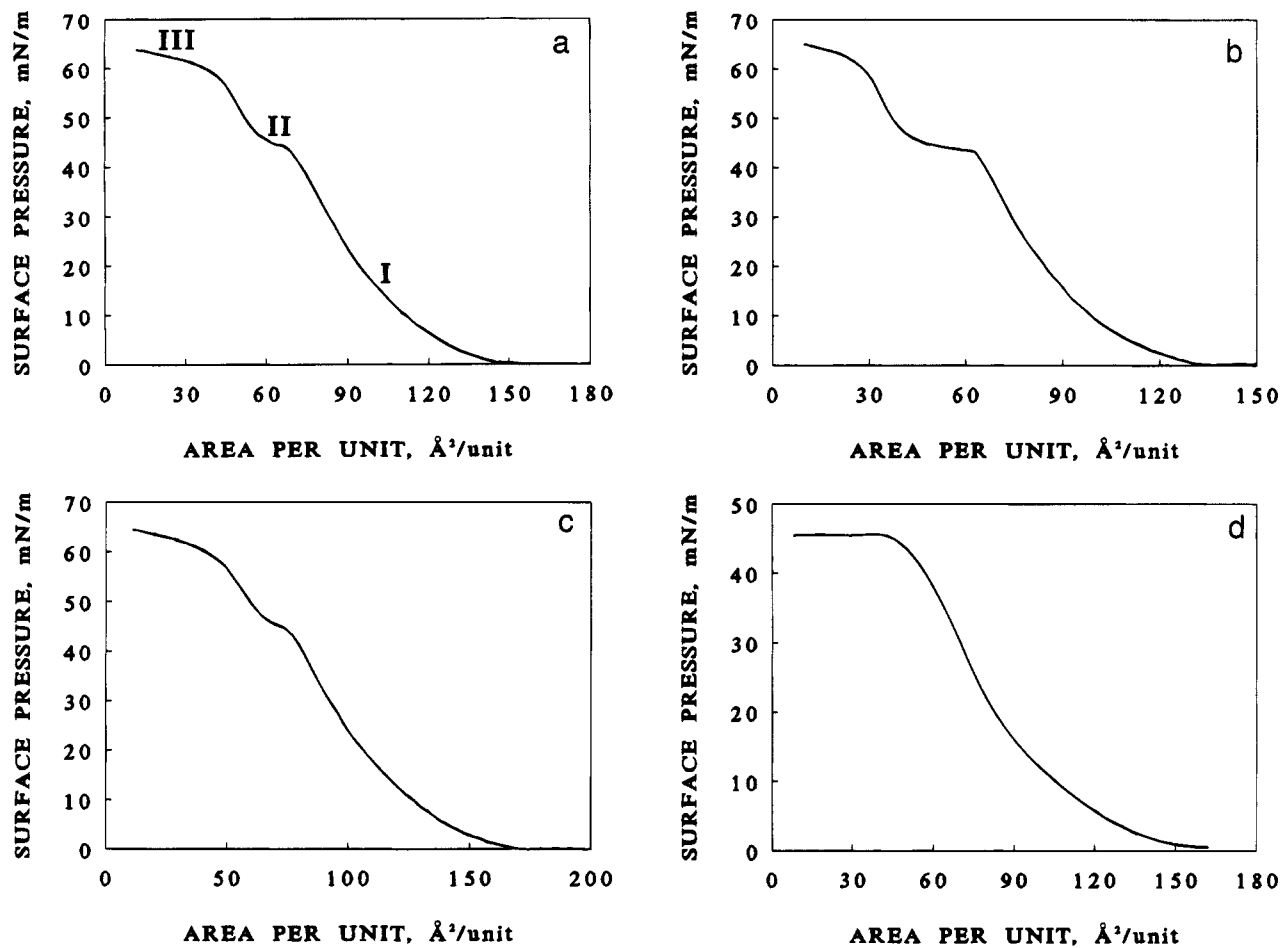
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**Figure 1.** Surface pressure vs surface area isotherms of the films which were prepared from stock solutions of 60-Å-diameter Pd/DDAC (a), 30-Å-diameter Pt/DDAC (b), and 60-Å-diameter Pt:Pd/DDAC (c) particles and of DDAC (d) in chloroform.

to increase the critical surface pressure which they can sustain.

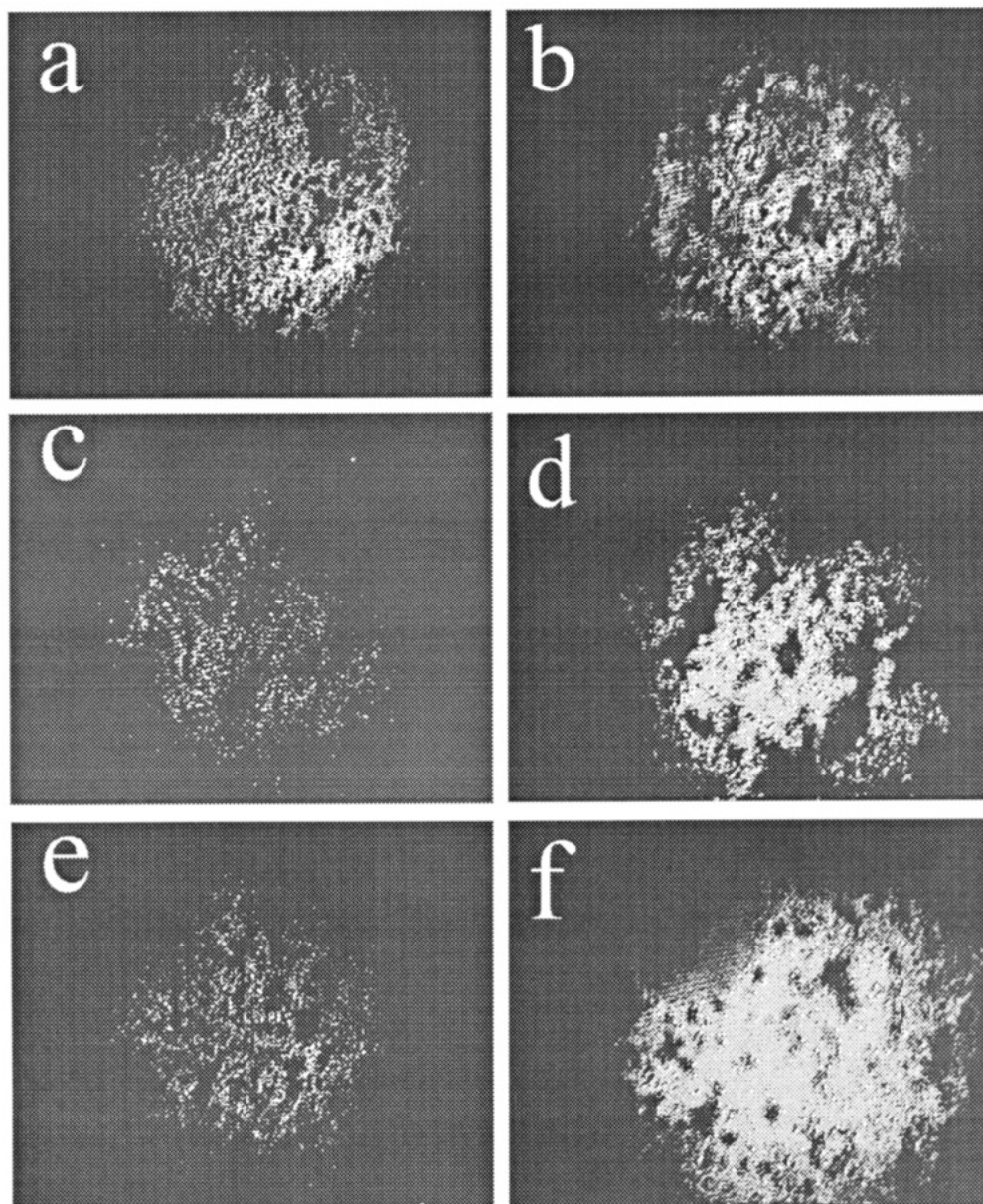
Comparison of Figures 1a and 1c shows the  $\Pi$  vs  $A$  isotherms of the Pd/DDAC and Pt:Pd/DDAC particulate films to be very similar. Both have short plateau regions (of 5–10 Å<sup>2</sup>/unit in length) at surface pressures of 45 mN/m and collapse completely at 65 mN/m. The Pt:Pd/DDAC isotherm is shifted slightly toward higher surface concentrations as compared with the Pd/DDAC curve. The  $\Pi$  vs  $A$  isotherm deriving from the Pt/DDAC particulate film exhibits a much longer plateau region (Figure 1b) than that observed for the Pd/DDAC particulate film (Figure 1a). Onset of the plateau begins at approximately 65 Å<sup>2</sup>/unit and terminates at 40 Å<sup>2</sup>/unit. Again, final collapse occurs at about 65 mN/m.

The difference between Pt, Pt/Pd, and Pd particle sizes is likely to be responsible for the observed  $\Pi$  vs  $A$  isotherms of the films examined. The value of the surface area at the onset of final collapse ( $\Pi = 65$  mN/m) can be referred to as an analogue of the limiting surface area of surfactant monolayers. Ultimately, for hexagonally close-packed (HCP) structures, as was observed for CdS and TiO<sub>2</sub> particulate films,<sup>6</sup> it is supposed to approach  $2\sqrt{3}R^2$ , where  $R$  is the particle radius. In the case of Pt, Pd, and Pt/Pd particles, the limiting area is expected to be substantially greater than that of HCP structures, due to a substantial contribution of surfactant molecules, even for highly compressed films. Most likely, the surfactant molecules participate

in a dynamic sorption/desorption process involving metal particles and the water surface. Eventually, the characteristics of the particle surface, being defined in the course of synthesis, determine the size of the pool of surfactant molecules that is necessary to keep them afloat.

Factors affecting the shape of the  $\Pi$  vs  $A$  curves in the particulate systems include (a) the amount of surfactant adsorbed on the water surface and on the particle surface, (b) the density of derivatization, (c) the particle–particle interactions due to capillary and hydrophobic forces, and (d) the mobility of the particles and, thus, their tendency to form a new phase. Monoparticulate film formation is the consequence of a delicate balance between the hydrophobic and hydrophilic properties of the particles. The particles ought not to be too hydrophilic; otherwise, they cannot stay on water surfaces. On the other hand, the excessively strong hydrophobic interaction would result in a strong interparticle aggregation.

The structure of the particulate films formed from Pt/DDAC, Pd/DDAC, and Pt:Pd/DDAC was investigated *in situ* on the water subphase by using BAM (Figure 2). Images taken at low compressions are shown in Figure 2a,c,e and those taken at higher compressions are shown in Figure 2b,d,f. Note that, although barely visible on the water surface by eye, the films can be readily viewed, even at low compression, by BAM. The quite good contrast obtained in the particulate film images was primarily due to the presence of the highly



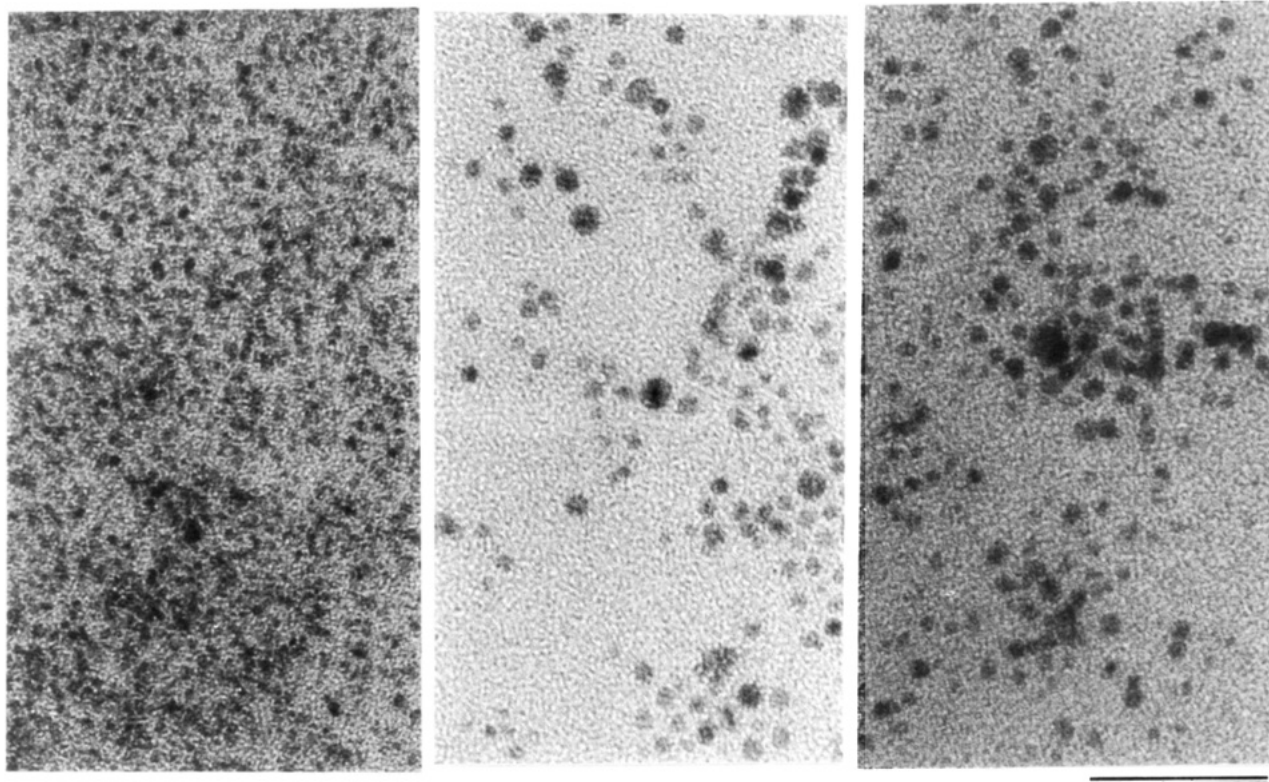
**Figure 2.** Brewster-angle microscopic images of the particulate films which were prepared from Pt/DDAC (a and b) and Pt:Pd/DDAC (c and d) and (e and f) at surface concentrations of  $150 \text{ \AA}^2/\text{surfactant unit}$  (a, c, and e) and  $50 \text{ \AA}^2/\text{surfactant unit}$  (b, d, and f). The dimensions of the rectangular images are 2.00 mm by 1.5 mm.

reflective metal colloid particles. BAM images also showed the domain structure of the films. Initially, quite broadly spread metal particles formed a new, denser phase upon compression. As was mentioned earlier, this transition is reflected as a plateau in the  $\Pi$  vs  $A$  isotherms. Compression increased the reflectivity of the films, as is expected upon decrease of the average interparticle separation by extrusion of the surfactant from the film.

TEM was utilized to investigate the structure of the films at a higher magnification. As was stated in the Methodology section, analysis of the film structure by TEM was complicated by difficulties which were encountered in the production of samples for microscopy. Poor transfer of the particulate films to the sample grids was obtained at low and moderate surface pressures. Thus, samples were produced only at high compressions; the images presented below were reproducible, however, and are representative of the whole area of the TEM sample. An electron micrograph of the Pt/DDAC film

at a surface concentration of  $50 \text{ \AA}^2/\text{surfactant}$  is shown in Figure 3a. The particles are of diameters of approximately  $30 \text{ \AA}$  and have very narrow size distributions. Although not close-packed, a fairly uniform coverage of the particles over the sample grid is apparent. Images of the Pd/DDAC and Pt:Pd/DDAC films are shown in Figure 3b,c. Both types of particles are larger than the pure Pt colloids, displaying diameters of approximately  $60 \text{ \AA}$ . Again, although not close-packed, the particles are distributed over the area of the macroscopic domains ( $1\text{--}2 \text{ mm}$ ) observed by BAM. It seems likely that while the majority of the surfactant molecules are not bound to the particles, there is a primary layer of surfactant associated with the metal colloid in a "micellar" type of arrangement. This "shell" of stabilizing surfactant prevents close approach of the particles. Thus, the final structure of the compressed film will be determined largely by particle-particle interactions, while for that of the expanded films ( $\Pi = 0$ ), particle-surfactant interactions will probably have





**Figure 3.** Transmission electron micrographs of the particulate films of Pt/DDAC (a, left), Pd/DDAC (b, middle), and Pt:Pd/DDAC (c, right) samples which were prepared at surface concentrations of  $50 \text{ \AA}^2/\text{surfactant unit}$ . All micrographs are shown at the same magnification (the scale bar = 50 nm).

the primary contribution because of long interparticle distances.

Fitting the reflectivity<sup>17</sup> data yielded film thicknesses and refractive indexes of  $d = 28 \pm 5.1 \text{ \AA}$  and  $n = 1.6 \pm 0.28$  for the Pt/DDAC film;  $d = 35.5 \pm 7.5 \text{ \AA}$  and  $n = 1.97 \pm 0.35$  for the Pd/DDAC film; and  $d = 28 \pm 6.3 \text{ \AA}$  and  $n = 2.0 \pm 0.45$  for the Pt:Pd/DDAC film. The thickness of the Pt/DDAC particulate film, as determined by the reflectivity measurements, is very near to the true particle diameter; this is consistent with the closer packing of the colloids in the film (Figure 3a). The closeness in the values of film thickness for different particles is likely to be connected with the contribution of surfactant molecules to the total film thickness reading, which may compensate for the greater particle diameter.

Metal colloid/surfactant films were transferred to solid substrates. Due to the high film viscosities, very slow dipping rates (in the order of 0.1 cm/s) were found to be essential for the production of good-quality films. The suitability of both glass and silanized glass substrates as supporting media for the films was investigated. It was demonstrated, by analysis of transfer ratios, that X-type films were deposited on silanized glass and Z-type films were deposited on regular glass substrates. In both cases, transfer ratios which were determined

for the first two layers were between 0.95 and 1.0. The efficiency of transfer then diminished with the deposition of a larger number of layers.

### Conclusion

Films of colloidal Pt, Pd, and mixed Pt:Pd = 1:1 particles have been produced. The solvent extraction/reduction method was followed in order to synthesize the particles; it constitutes a very general technique for the preparation of small, uniform metal crystallites. It was shown that a considerable part of the surfactant molecules that were used to synthesize metal nanoparticles and to stabilize them on water surfaces could be extruded from the interface film during compression. A significant amount of the stabilizer was incorporated, even in highly compressed monoparticulate films, preventing a completely close-packed arrangement of the metal particles. A domain consisting of pure surfactant molecules was observed at all stages of compression. All metal colloids exhibited similar behavior upon being spread on water surfaces.

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