

# Kinetics of the Formation of Nano-Sized Platinum Particles in Water-in-Oil Microemulsions

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The effect of surfactant type and temperature on the kinetics of the formation of platinum nanoparticles in water-in-oil microemulsions by chemical reduction of  $\text{PtCl}_6^{2-}$  were examined with time-resolved UV-vis absorption spectroscopy. The surfactants used were poly(ethylene glycol)monododecyl ethers ( $\text{C}_{12}\text{E}_4$ ,  $\text{C}_{12}\text{E}_5$ ,  $\text{C}_{12}\text{E}_6$ ), sodium bis(2-ethylhexyl)sulphosuccinate (AOT), and mixtures of the alcohol ethoxylates and AOT. The oil domain was *n*-heptane. The microemulsion droplet size was measured by a dynamic light scattering technique (photon correlation spectroscopy) and the final platinum particle size was determined by transmission electron microscopy. The reaction rate for platinum particle formation was approximately the same in microemulsions based on either of the alcohol ethoxylates but considerably lower for microemulsions based on AOT. In microemulsions based on mixtures of an alcohol ethoxylate and AOT the reaction rate was similar to that obtained when alcohol ethoxylate was the sole surfactant. The reaction was observed to be particularly rapid in microemulsions based on combinations of AOT and  $\text{C}_{12}\text{E}_5$  or  $\text{C}_{12}\text{E}_6$ , and the rate was relatively independent of the ratio of the nonionic and anionic surfactants. The reaction was found to be of first order for platinum nanoparticles formed in alcohol ethoxylate-, AOT- $\text{C}_{12}\text{E}_5$ -, and AOT- $\text{C}_{12}\text{E}_6$ -based microemulsions, whereas in microemulsions with AOT and AOT- $\text{C}_{12}\text{E}_4$  the reaction rate seemed to be of higher reaction order. The platinum particles were found to be less than 5 nm in average diameter, which was consistent with the microemulsion droplet size. © 2001 Academic Press

**Key Words:** nanoparticle formation; platinum; w/o microemulsion; reaction rate; droplet size; particle size; nonionic surfactants; AOT.

## INTRODUCTION

Nanoparticle technology is of substantial interest for a large number of practical applications. In this connection, catalysis represents one of the single most important applications of nanotechnology. In order to achieve a deeper understanding of details in reaction mechanisms and kinetics of catalytic processes, a

well-defined catalyst is an indispensable tool. Traditionally, supported catalysts have been produced by wet impregnation using water-soluble metal salts, which results in well-dispersed catalysts with high activity and good thermal stability. The particle size of the active phase is usually in the nanometer range but with a quite broad size distribution and a low degree of control over the particle size. This renders the interpretation of, for example, size-dependent mechanistic phenomena of the catalyst impossible.

As reported by Johansson *et al.* (1) and Wong *et al.* (2), catalyst samples with platinum nanoparticles of specific size and shape, organized in a pattern on silica-ceria and alumina-ceria supports, have been prepared by electron beam lithography (EBL) and tested for catalytic activity in a microreactor. With this technique one can prepare geometrically well-defined model catalysts, which makes studies of geometrically dependent phenomena, such as spill-over effects and particle-size-dependent reactions possible. Another route to prepare nanosized particles is to use a water-in-oil (w/o) microemulsion where a platinum precursor is reduced to metallic platinum in the water pools. With this method of preparation, particles with relatively narrow size distribution down to an average of a few nanometers can be obtained (3–7). At least in some systems it has been found that not only the size but also the shape of the particles can be controlled (8, 9).

To prepare catalysts with nanoparticles of specific size and shape, it is important to understand the fundamentals of particle formation in microemulsions. The main objective of this work was to investigate how the type of surfactant and the reaction temperature affect the kinetics of the particle formation in microemulsions. A secondary objective was to study how the particle size is affected by the type of surfactant used in the formulation and by the platinum concentration in the water pool of the w/o microemulsion.

## EXPERIMENTAL PROCEDURE

### Chemicals

The alcohol ethoxylates, tetra(ethylene glycol)monododecyl ether ( $\text{C}_{12}\text{E}_4$ ), penta (ethylene glycol)monododecyl ether

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(C<sub>12</sub>E<sub>5</sub>) and hexa(ethylene glycol)monododecyl ether (C<sub>12</sub>E<sub>6</sub>) were homologue pure surfactants from NIKKOL, Japan. Sodium bis(2-ethylhexyl)sulphosuccinate (AOT) (99%), hexachloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>) (99.995%), sodium borohydride (NaBH<sub>4</sub>) (98%), and *n*-heptane (99%) were purchased from Sigma-Aldrich. All chemicals were used as received, without further purification.

### Platinum Particle Synthesis

The platinum particles were prepared in microemulsions containing *n*-heptane as oil component, water, and 15 wt% surfactant. The surfactants used were C<sub>12</sub>E<sub>4</sub>, C<sub>12</sub>E<sub>5</sub>, C<sub>12</sub>E<sub>6</sub>, or AOT, or a mixture of a nonionic surfactant and AOT. The *n*-heptane and the surfactant were mixed and an aqueous solution of the Pt complex, [Pt<sup>+IV</sup>Cl<sub>6</sub>]<sup>2-</sup>, was subsequently added to form a microemulsion with the Pt complex in the water pools. The water-to-surfactant molar ratio was equal to 4 and the aqueous component contained 0.2, 0.5, or 3 wt% Pt. A microemulsion, of the same composition of oil, water, and surfactant that contained the reducing agent (NaBH<sub>4</sub>) in a molar ratio of 1:15 to H<sub>2</sub>O, was also prepared. This microemulsion was then added to the microemulsion with the Pt complex, in an amount corresponding to 5 moles of NaBH<sub>4</sub> per mole of Pt, whereby the Pt complex was reduced to Pt particles. All reactions were carried out at 25°C if not otherwise stated.

### UV-Vis Spectroscopy

In aqueous solution, the platinum complex (PtCl<sub>6</sub><sup>2-</sup>) absorbs UV at 201 and 261 nm (10, 11) and metallic platinum particles absorb UV at 215 nm (12). A w/o microemulsion containing PtCl<sub>6</sub><sup>2-</sup> in the water pool absorbs UV at 260–270 nm (12). When particles are formed in the microemulsion, the 260–270 nm peak attributed to the platinum complex disappears and a peak due to metallic Pt particles appears.

Time-resolved (6 scans/min) UV-vis absorption spectroscopy (HP 8453 UV-Visible Spectrophotometer) was used to monitor the reaction in the microemulsions. The platinum complex-containing microemulsion (0.2 wt% Pt) was prepared as described previously and placed into a cuvette in the UV spectrometer. A microemulsion containing the reducing agent was subsequently added to the cuvette (approximately 3 ml Pt complex microemulsion and 0.5 ml microemulsion with NaBH<sub>4</sub>) and the absorption was measured continuously during the reaction. A microemulsion containing only *n*-heptane, surfactant, and water was used as reference sample and absorption data for the other samples were appropriately corrected.

### Photon Correlation Spectroscopy (PCS)

Microemulsions were prepared as described above. Photon correlation spectroscopy (which is a dynamic light-scattering method) measurements were carried out on microemulsions without platinum complex (only oil, surfactant, and water) and on microemulsions containing platinum complex (0.5 and

3 wt% Pt) in the water pools. Measurements were also performed on the reaction mixture after reduction of the platinum complex to metallic platinum. The PCS measurements were carried out at room temperature (25.0 ± 0.1°C). A frequency doubled Nd:VAN laser (Coherent Inc.), operating at 532.0 nm with a typical output power in the range 5–25 mW, provided the incident radiation. The vertically polarized scattered light was collected and divided into two equal parts by a prism and fed to two photomultiplier tubes (PMTs). Using two PMTs and performing subsequent cross-correlation eliminates erroneous correlation due to afterpulsing of each individual PMT. The signal was sent to a correlator (ALV-5000/FAST) which calculates the normalized intensity autocorrelation function,  $g(q, t)$ , over 12 decades in time from 10<sup>-8</sup> to 10<sup>4</sup> s. The experimentally determined correlation function is, in a homodyne experiment (13), related to the intermediate scattering function according to  $S(q, t) \propto \sqrt{g(q, t) - 1}$  (13–15). A characteristic relaxation time,  $\tau$ , can then be determined by curve fitting with

$$S(q, t) = A \exp(-t/\tau). \quad [1]$$

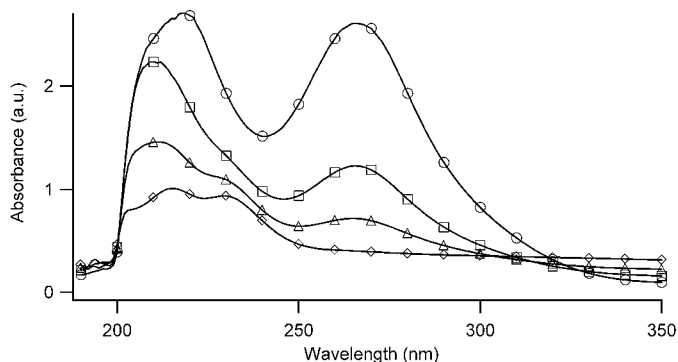
### Transmission Electron Microscopy (TEM)

Platinum nanoparticles were prepared in w/o microemulsions as described previously. The aqueous component contained 0.5 or 3 wt% Pt. A droplet of the particle suspension was deposited on a carbon-coated copper grid and TEM studies of the platinum nanoparticles were subsequently performed on a JEOL 200 CX electron microscope at an operating voltage of 200 kV. All the measurements were carried out 1 or 2 days after the platinum nanoparticles were formed.

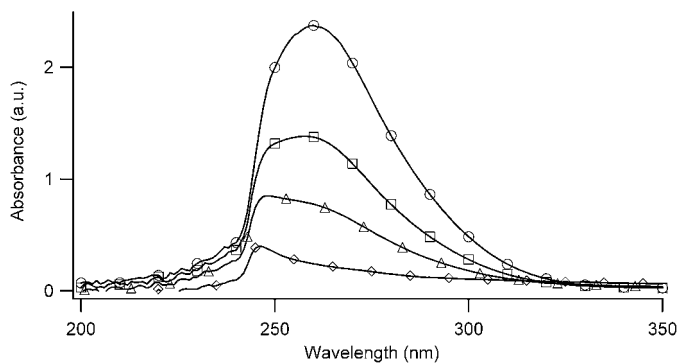
## RESULTS

### Rate of Platinum Particle Formation

The UV spectra differed depending on which surfactant was used in the microemulsion formulation. The microemulsions based on nonionic surfactant as sole surfactant (see Fig. 1) had two peaks (around 265 nm and 220–225 nm) before reduction.



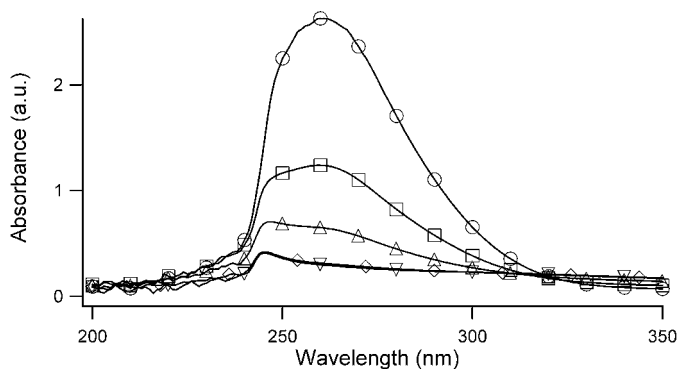
**FIG. 1.** UV absorption spectra recorded during reduction in a microemulsion based on the nonionic surfactant C<sub>12</sub>E<sub>5</sub>. Before reduction (○), after 2 min of reduction (□), after 4 min of reduction (△), and after 7 min of reduction (◇).



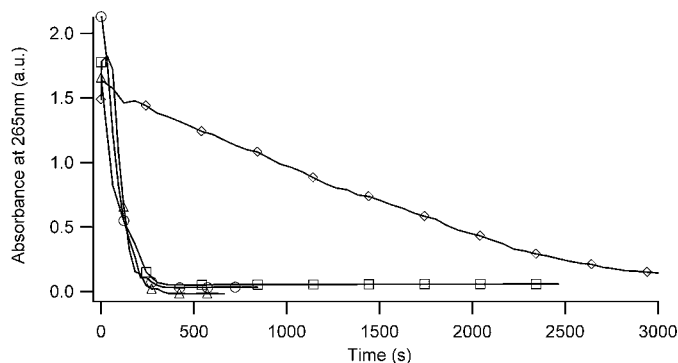
**FIG. 2.** UV absorption spectra recorded during reduction in an AOT-based microemulsion. Before reduction ( $\circ$ ), after 15 min of reduction ( $\square$ ), after 30 min of reduction ( $\triangle$ ), and after 50 min of reduction ( $\diamond$ ).

As the reaction progressed, these peaks decreased and a peak around 230 nm started to appear. The microemulsions based on AOT as sole surfactant or mixed with nonionic surfactants (see Figs. 2 and 3) showed one peak (260–270 nm) before reduction. During the reaction a shift in this peak toward 245 nm was observed. As all UV spectra initially showed a peak around 265 nm, the decrease of this peak was monitored as a function of time and used as a measure of the kinetics of Pt particle formation (11).

The UV analyses showed that the reaction rate was higher in a microemulsion based on alcohol ethoxylate than in one based on AOT (see Fig. 4). The reaction took about the same time (around 5 min) in a microemulsion with either of the alcohol ethoxylates, while a microemulsion with AOT required approximately 50 min to reach completion. In microemulsions based on mixtures of AOT and  $C_{12}E_5$  or  $C_{12}E_6$  (see Fig. 5), the reaction rate was similar or slightly higher than in a microemulsion with an alcohol ethoxylate as sole surfactant. Approximately the same reaction rate was obtained regardless of the ratio of AOT to  $C_{12}E_5$  within the concentration range studied. The reaction seemed to be much slower in a microemulsion based on a mix-



**FIG. 3.** UV absorption spectra recorded during reduction in a microemulsion based on a mixture of AOT and  $C_{12}E_5$  (75 : 25 by weight). Before reduction ( $\circ$ ), after 0.5 min of reduction ( $\square$ ), after 1 min of reduction ( $\triangle$ ), after 2 min of reduction ( $\diamond$ ), and after 30 min of reduction ( $\nabla$ ).



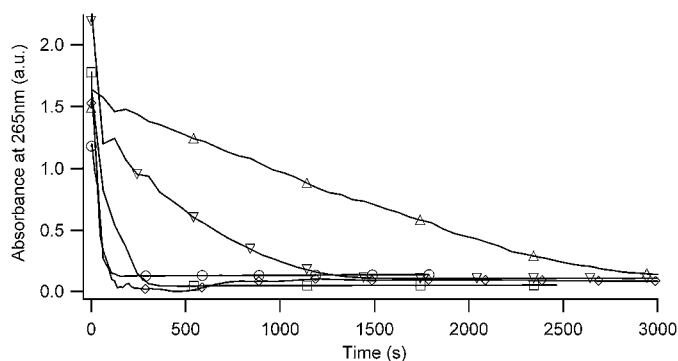
**FIG. 4.** Absorbance at 265 nm vs time. Comparison of reaction rate for microemulsions based on  $C_{12}E_4$  ( $\circ$ ),  $C_{12}E_5$  ( $\square$ ),  $C_{12}E_6$  ( $\triangle$ ), and AOT ( $\diamond$ ).

ture of AOT and  $C_{12}E_4$ , as can be seen in Fig. 5. The reaction rate increased with increasing temperature, as expected, and the effect was most pronounced at lower temperatures and the rate leveled off above  $35^\circ\text{C}$ , as can be seen from Fig. 6.

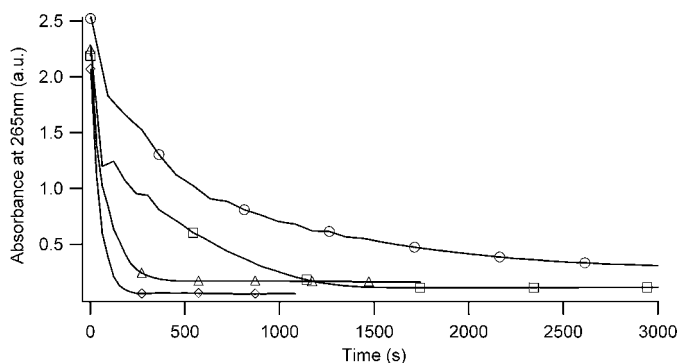
The reaction order was calculated by plotting  $\ln(A_t - A_\infty)$  vs time (16) during the reduction, where  $A_t$  is the absorbance (at 265 nm) at time  $t$  and  $A_\infty$  is the absorbance (at 265 nm) obtained after the reduction was completed. The reactions seemed to be first order for reduction in alcohol ethoxylate-, AOT- $C_{12}E_5$ -, and AOT- $C_{12}E_6$ -based microemulsions, whereas the reactions in microemulsions with AOT and AOT- $C_{12}E_4$  seemed to be of higher reaction orders.

#### Size of Microemulsion Droplets and of Platinum Particles in Solution

Nanosized particles dispersed in a low viscosity solvent diffuse fast. In order to experimentally determine the diffusive properties of nanosized particles using PCS, a reliable probing of fast processes is necessary. The combination of fast hardware to calculate the correlation function and the PMT detection system used in the present experimental setup enables reliable



**FIG. 5.** Absorbance at 265 nm vs time. Comparison of reaction rate for microemulsions based on  $C_{12}E_5$  ( $\square$ ), AOT ( $\triangle$ ), and mixtures of 50 wt% AOT and 50 wt%  $C_{12}E_4$  ( $\nabla$ ), 75 wt% AOT and 25 wt%  $C_{12}E_5$  ( $\circ$ ), and 50 wt% AOT and 50 wt%  $C_{12}E_6$  ( $\diamond$ ).



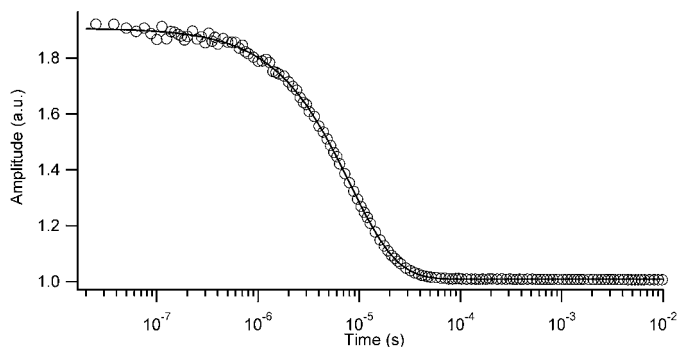
**FIG. 6.** Absorbance at 265 nm vs time. Comparison of reaction rate at different temperatures in a microemulsion based on 50 wt%  $C_{12}E_4$  and 50 wt% AOT. 15°C ( $\circ$ ), 25°C ( $\square$ ), 35°C ( $\triangle$ ), and 45°C ( $\diamond$ ).

determination of particle sizes down to the order of nanometers. The reproducibility of the experiments was proven from a series of measurements performed at identical conditions on a microemulsion based on  $C_{12}E_5$ . The standard deviation calculated from these measurements was 0.1 nm, which indicated high reliability for the measurements since the hydrodynamic radius of the droplets were of the order of a few nanometers.

The diffusion constant,  $D$ , can be obtained from the PCS experiments (see Fig. 7) using  $D = 1/\tau q^2$  with  $q = (4\pi n/\lambda) \sin(\theta/2)$ , where  $n$  is the refractive index of the solvent ( $n$ -heptane),  $\lambda$  is the incident wavelength, and  $\theta$  is the scattering angle (13–15). The hydrodynamic radius can then be calculated using the Stoke–Einstein relation (17)

$$D_o = k_B T / 6\pi \eta r, \quad [2]$$

where  $D_o$  is the diffusion constant at infinite dilution,  $k_B$  is Boltzmann's constant,  $T$  is temperature,  $\eta$  is the viscosity of the solvent ( $n$ -heptane), and  $r$  is the hydrodynamic radius of the microemulsion droplets. Under the present experimental conditions the following parameter values were used:  $\lambda = 532$  nm,  $T = 25^\circ\text{C}$ ,  $\eta = 0.42 \times 10^{-3}$  Pa·s (18),  $n = 1.388$  (18), and



**FIG. 7.** PCS measurement on a microemulsion based on  $C_{12}E_5$  ( $\circ$ ) and the fit according to Eq. [1] (solid line). Relaxation time,  $\tau$ , can be calculated from the fit-function.

$\theta = 90^\circ$ . Since Stoke–Einstein's relation is strictly applicable only at infinite dilution, the experimentally determined diffusion constant,  $D$ , needs to be compensated for interaction between the particles. For this purpose, the equation (19, 20)

$$D = D_o(1 + \alpha\phi), \quad [3]$$

where  $\alpha$  is the diffusional virial coefficient, can be used if the volume fraction of the dispersed phase,  $\phi$ , is small enough ( $\phi \lesssim 0.1$ ) (19), which was the case in the present work. The constant  $\alpha$  has previously been determined by Hou *et al.* for similar systems (20) and based on their work we have estimated  $\alpha = 0.4$  for the present conditions. With this  $\alpha$  value the correction of the hydrodynamic radii, obtained in this work, was less than 5%. The small particle interaction influence was probably related to the low water content ( $\phi_{aq} \leq 0.02$ ) in the system (21).

The PCS measurements on microemulsions resulted in relaxation times which corresponded to hydrodynamic radii in the size range of 2.3–6.5 nm (see Table 1). Evaluation of the data revealed monodispersity for most of the samples but for a few samples a size distribution up to  $\pm 35\%$  was observed. One may observe from Table 1 that the hydrodynamic radius was slightly increased when the polyoxyethylene chain length was increased for microemulsions based on nonionic surfactant as sole surfactant. It can also be seen that the radius of these droplets with Pt complex in the water pools was similar or slightly increased compared to droplets without platinum complex. For the microemulsions based on AOT (both as sole surfactant and mixed with nonionic surfactant), in contrast, the presence of Pt complex in the water pools resulted in slightly decreased hydrodynamic radius.

A PCS measurement carried out on a platinum particle suspension resulted in a relaxation time,  $\tau$ , of  $2.48 \times 10^{-4}$ , which corresponds to a hydrodynamic radius of 69 nm. The fact that the hydrodynamic radius was significantly larger for the platinum

**TABLE 1**  
**Relaxation Time ( $\tau$ ), Diffusion Coefficient ( $D$ ), and Corresponding Hydrodynamic Radius of the Microemulsion Droplets ( $r$ ) Obtained from PCS Measurements**

Sample	$\tau$ (s)	$D$ ( $\text{m}^2/\text{s}$ )	$r$ (nm)
$C_{12}E_4$ , $H_2O$	$1.11 \times 10^{-5}$	$1.68 \times 10^{-10}$	3.1
$C_{12}E_4$ , 0.5 wt% Pt	$1.09 \times 10^{-5}$	$1.70 \times 10^{-10}$	3.1
$C_{12}E_5$ , $H_2O$	$1.50 \times 10^{-5}$	$1.24 \times 10^{-10}$	4.2
$C_{12}E_5$ , 0.5 wt% Pt	$1.55 \times 10^{-5}$	$1.20 \times 10^{-10}$	4.3
$C_{12}E_5$ , 3 wt% Pt	$1.59 \times 10^{-5}$	$1.17 \times 10^{-10}$	4.4
$C_{12}E_6$ , $H_2O$	$2.10 \times 10^{-5}$	$8.87 \times 10^{-11}$	5.9
$C_{12}E_6$ , 0.5 wt% Pt	$2.33 \times 10^{-5}$	$7.97 \times 10^{-11}$	6.5
AOT, $H_2O$	$1.12 \times 10^{-5}$	$1.66 \times 10^{-10}$	3.1
AOT, 0.5 wt% Pt	$9.93 \times 10^{-6}$	$1.87 \times 10^{-10}$	2.8
25 wt% $C_{12}E_5$ –75 wt% AOT, $H_2O$	$8.87 \times 10^{-6}$	$2.14 \times 10^{-10}$	2.4
25 wt% $C_{12}E_5$ –75 wt% AOT, 0.5 wt% Pt	$8.23 \times 10^{-6}$	$2.26 \times 10^{-10}$	2.3

**TABLE 2**  
**Average Radius of Discrete Pt Particles Measured by TEM**  
**Obtained from Microemulsions Based on Different Surfactants**

Sample	Average radius (nm)
C <sub>12</sub> E <sub>4</sub> , 0.5 wt% Pt	1.9
C <sub>12</sub> E <sub>4</sub> , 3 wt% Pt	2.3
C <sub>12</sub> E <sub>4</sub> , 3 wt% Pt, aged 2 days	2.2
50 wt% C <sub>12</sub> E <sub>4</sub> & 50 wt% AOT, 0.5 wt% Pt	2.4
C <sub>12</sub> E <sub>5</sub> , 0.5 wt% Pt	2.0
C <sub>12</sub> E <sub>5</sub> , 3 wt% Pt	2.5
75 wt% C <sub>12</sub> E <sub>5</sub> & 25 wt% AOT, 0.5 wt% Pt	1.7
50 wt% C <sub>12</sub> E <sub>5</sub> & 50 wt% AOT, 0.5 wt% Pt	1.2
25 wt% C <sub>12</sub> E <sub>5</sub> & 75 wt% AOT, 0.5 wt% Pt	1.0
C <sub>12</sub> E <sub>6</sub> , 0.5 wt% Pt	1.5
C <sub>12</sub> E <sub>6</sub> , 3 wt% Pt	2.2
50 wt% C <sub>12</sub> E <sub>6</sub> & 50 wt% AOT, 0.5 wt% Pt	1.4
AOT, 0.5 wt% Pt	1.2

Note. All samples, unless otherwise stated, were aged for 1 day.

particles in the particle suspension than for the corresponding microemulsion droplets indicated that the platinum particles seemed to undergo gradual agglomeration. This was also observed by TEM, where some of the micrographs showed agglomerates of discrete particles. Another factor that might influence the particle stability (resulting in formation of agglomerates) was that the particle suspension had to be diluted prior to the PCS measurement.

The PCS measurements result in hydrodynamic radii, that are different from the radii obtained from TEM. The hydrodynamic radius includes the surfactant monolayer and hence should be slightly larger than the radius obtained by TEM. However, one should be able to reliably compare hydrodynamic radii for the different microemulsion droplets with a high degree of accuracy.

#### Size of Platinum Particles

The TEM micrographs showed that reduction in the microemulsion systems resulted in particles with average diameters less than  $5 \pm 1$  nm. The smallest particles (2 nm in average diameter) were obtained from the microemulsion based on C<sub>12</sub>E<sub>5</sub> : AOT (25 wt% : 75 wt%) with 0.5 wt% Pt in the aqueous domain. Inspection of the particle size after aging (room temperature) for one and two days gave similar results, which indicated that aging had no significant effect on the particle size, as has also been reported by, e.g., Chen *et al.* (22). Addition of the reducing agent as an aqueous solution gave slightly larger particles, which was probably because the water-to-surfactant molar ratio was increased as compared with addition of the reducing agent in a microemulsion.

Particles prepared in microemulsions containing only alcohol ethoxylate as surfactant seemed to increase in size as the PtCl<sub>6</sub><sup>2-</sup> concentration in the aqueous component was increased. The influence of the type of surfactant used on the discrete particle size is shown in Table 2. As can be seen, there was no dramatic difference in size among the different surfactants and surfactant

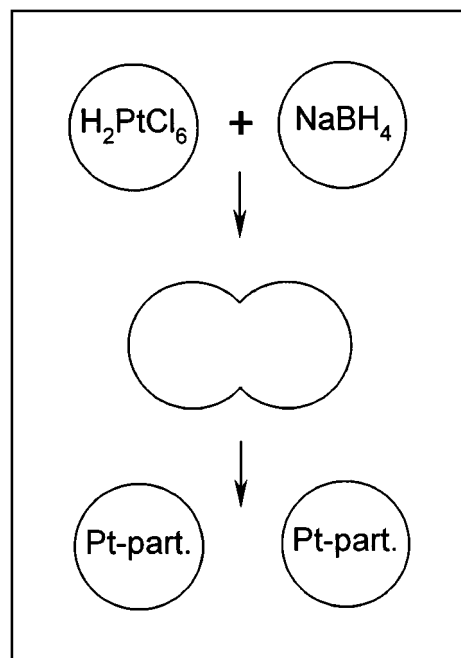
combinations. Evidently the events that led to termination of particle growth seemed not to depend much on the charge of the surfactant headgroup. In some TEM micrographs agglomeration was observed; however, it is not obvious that it was the formation in microemulsion that led to agglomeration. The agglomeration may also have been caused by the TEM-sample preparation.

## DISCUSSION

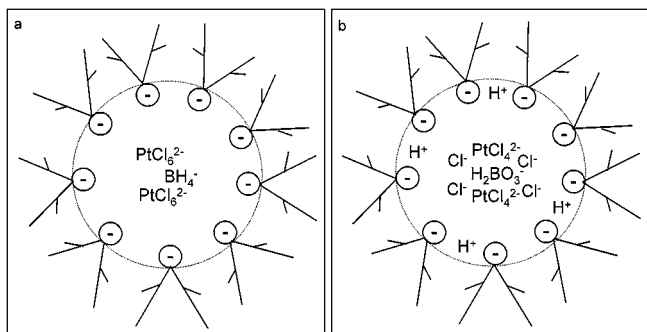
The UV absorption measurements show that the platinum particle formation is much more rapid in microemulsions based on an alcohol ethoxylate than on AOT. The process involves mixing of two microemulsions, one containing the platinum complex and one containing the reducing agent. Since reduction of PtCl<sub>6</sub><sup>2-</sup> by diffusion of BH<sub>4</sub><sup>-</sup> through the oil continuous domain is rather unlikely, the fusion of droplets (see Fig. 8) is a prerequisite for the reaction to proceed and may be the rate-determining step in the reduction of PtCl<sub>6</sub><sup>2-</sup> to metallic platinum. Alternatively, the difference in rate of particle formation may be due to a difference in the microenvironment within the fused water droplets of the microemulsion that form after mixing of the two reactant systems (see Fig. 9). The two alternatives are discussed below.

#### Fusion of Water Droplets

The rate of droplet fusion is likely to be governed by the type of surfactant that forms the palisade layer at the oil–water interface. However, it is not self-evident which of the two types of surfactants, AOT or an alcohol ethoxylate, would give the highest rate of fusion. The anionic surfactant AOT is much less soluble in the



**FIG. 8.** Schematic illustration of the droplet fusion.



**FIG. 9.** Schematic illustration of the microenvironment within a fused AOT-based microemulsion droplet, i.e., after mixing of the two initial microemulsions: (a) the left-hand side of Reaction [8] and (b) the right-hand side of Reaction [8].

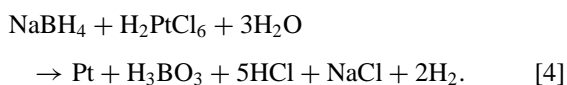
continuous hydrocarbon domain than the nonionic surfactants used. The high solubility of the alcohol ethoxylates in the continuous domain will lead to a flux of surfactant molecules back and forth between the bulk hydrocarbon domain and the droplet interface. This process will work against tight and ordered packing of alcohol ethoxylates and can consequently be expected to favor droplet fusion. In contrast, the water droplets stabilized by AOT can be regarded as hard spheres, which may lead to more elastic collisions and slower rate of fusion of droplets (23). However, according to Clint *et al.* (16) and Fletcher *et al.* (23) the exchange kinetics of AOT droplets occurs on a millisecond time scale.

The ratio of anionic and nonionic surfactant at the oil–water interface in mixed systems is likely to depend on the solubility of the surfactants in the continuous oil domain. As mentioned above, AOT has a low solubility in hydrocarbons. Alcohol ethoxylates are much more oil-soluble and C<sub>12</sub>E<sub>4</sub> in particular, with its short polyoxyethylene chain, has a high solubility in hydrocarbons. On the basis of the solubility one may thus expect the mixed surfactant film of the AOT–C<sub>12</sub>E<sub>4</sub> system to have a higher AOT to alcohol ethoxylate ratio than the surfactant film of the AOT–C<sub>12</sub>E<sub>5</sub> and AOT–C<sub>12</sub>E<sub>6</sub> systems. This would fit the observed relative reactivity, the AOT–C<sub>12</sub>E<sub>4</sub> system resembling the AOT system, and the AOT–C<sub>12</sub>E<sub>5</sub> and the AOT–C<sub>12</sub>E<sub>6</sub> systems resembling the alcohol ethoxylate systems.

#### Water Droplet Microenvironment

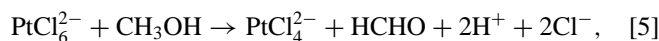
The second explanation to the observed difference in reaction rate between the different systems relates to the microenvironment within the microemulsion droplets that form after the two starting microemulsions have been mixed and the droplets have fused.

The chemical reduction of hexachloroplatinic acid by NaBH<sub>4</sub> has been suggested by Van Rheenen *et al.* (24) to proceed via the following overall reaction in aqueous solution:



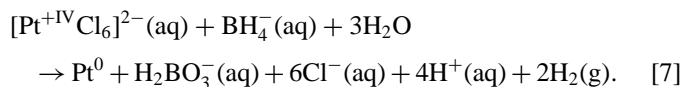
The authors (24) claim that platinum microcrystals catalyze the decomposition of NaBH<sub>4</sub> and consequently, a large excess of NaBH<sub>4</sub> is needed to completely reduce the hexachloroplatinic acid. The ratio of five moles of NaBH<sub>4</sub> per mole of H<sub>2</sub>PtCl<sub>6</sub>, which was used in this investigation, is probably sufficient for the reduction in nonionics-, AOT–C<sub>12</sub>E<sub>5</sub>-, and AOT–C<sub>12</sub>E<sub>6</sub>-based microemulsions since the absorbance decay of PtCl<sub>6</sub><sup>2-</sup> is close to exponential. This indicates that the reaction is of first order and hence limited by the PtCl<sub>6</sub><sup>2-</sup> concentration. However, higher reaction order is obtained for the reduction in AOT- and AOT–C<sub>12</sub>E<sub>4</sub>-based microemulsions, implying also that the supply of BH<sub>4</sub><sup>-</sup> is limited and hence influences the reaction rate for these systems.

Duff *et al.* (11) studied the reduction of hexachloroplatinic complex by methanol, in the presence of polyvinylpyrrolidone (PVP) as a steric stabilizer, in aqueous solution and proposed a two-step reaction:

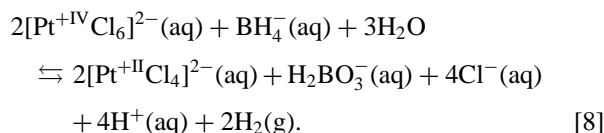


The PtCl<sub>4</sub><sup>2-</sup> complex formed in Reaction [5] has negligible absorption at 260 nm. However, according to Duff *et al.* (11) Reaction [6] proceeds much faster than Reaction [5], indicating that the disappearance of the peak at 260 nm from the UV spectrum can still be used to monitor the formation rate of metallic platinum. Addition of NaCl or HCl was found to slow down the reaction, suggesting that a high concentration of chloride ions retard the reduction of platinum complex to metallic platinum (11).

Taking the above mentioned reactions, [4]–[6], into account, we suggest the reaction inside the microemulsion water droplets to proceed via the following overall reaction:



However, one may assume that the reduction proceeds via several steps and in accordance with the two-step reduction of hexachloroplatinic complex by methanol (11), we propose the first step to proceed via the following reaction:



When the reaction occurs in the water droplets in an AOT-based microemulsion, it is likely that there will be an electrostatic repulsion among the negatively charged AOT sulfonate groups, the hexachloroplatinic complex, and the borohydride ions. This repulsion will cause a local increase in concentration of the two negatively charged reactants in the center of the water

droplets (see Fig. 9a). An increased reactant concentration can be assumed to cause an increase in reaction rate, which has for instance been demonstrated for the oxidation of iodide by persulfate using either AOT (25, 26) or sodium dodecylsulfate (27) as surfactant. However, as Reaction [8] proceeds the concentration of chloride ions will increase and in an AOT-based system the  $\text{Cl}^-$  ions will interact repulsively with the sulfonate headgroups, resulting in a local increase also of  $\text{Cl}^-$  ions in the core of the water droplet (see Fig. 9b). If Reaction [8] is regarded as an equilibrium reaction, an increased concentration of chloride ions is likely to shift the reaction equilibrium to the left. This will retard the formation of metallic platinum particles in an AOT-based system. When the reaction occurs in a nonionics-based microemulsion, however, there will be no electrostatic repulsion between the surfactant headgroups and the anions present in the water pools.

It is also conceivable that the difference in kinetics between the AOT- and the nonionics-based microemulsions is related to differences in the surfactant's ability to act as ligand in the platinum complex. Shelimov *et al.* (28) have studied the interaction between  $\text{PtCl}_6^{2-}$  and alumina in aqueous solution. The authors suggest several different mechanisms for this interaction, e.g., electrostatic adsorption of the hexachloroplatinic complex at the alumina surface and ligand substitution reactions, where alumina surface groups replace some of the initial ligands in the chloroplatinic complex. In the latter case, both OH-bridging ligands and Cl-bridging ligands are suggested. One can envisage ways in which the surfactant headgroups, both polyoxyethylene chains of nonionic surfactants and the sulfonate group of AOT, can interact with the platinum in the hexachloroplatinic complex. The interaction will differ depending on the type of surfactant, and the difference in binding between Pt and the ligands in the complex may influence the kinetics of the reaction inside the droplets.

### CONCLUDING REMARKS

In summary, we have discussed two different interpretations of the results obtained in this work. The difference in reactivity obtained with the AOT- and the nonionics-based microemulsions may be due to either the droplet fusion or the microenvironment within the fused water droplets. If the surfactant present at the oil-water interface were fairly soluble in the oil component, which is the case for the alcohol ethoxylates, the droplets can be assumed to fuse more readily than if the surfactant were insoluble in the oil domain. This means that the alcohol ethoxylates-based microemulsions would have a higher dynamics for droplet fusion than the AOT-based ones. The first-order reaction rate, obtained for reduction in nonionics-, AOT- $\text{C}_{12}\text{E}_5$ -, and AOT- $\text{C}_{12}\text{E}_6$ -based microemulsions, indicates that it is the chemical reduction of the hexachloroplatinic complex that is rate limiting rather than the supply of reducing agent. This implies that the droplet coalescence is fast enough for material transport between the water droplets in these systems. The higher rate order for reduction, obtained in AOT-

and AOT- $\text{C}_{12}\text{E}_4$ -based microemulsions, also indicates that the supply of reducing agent may affect the reaction rate in these systems.

The reaction rate may, however, also be governed by the microenvironment within the fused droplets, where an anionic surfactant will interact repulsively with the negatively charged reactants. As the reaction proceeds, chloride ions will form and in an AOT-based system repulsive interactions between the sulfonate headgroups and the chloride ions is likely to cause a local increase in  $\text{Cl}^-$  concentration in the core of the droplets. This, in turn, may retard the reduction of hexachloroplatinic complex to metallic platinum.

Since it is not immediately obvious which of mechanism governs the reaction rate, further studies involving nuclear magnetic resonance and photon correlation spectroscopy are planned to investigate, in more detail, the dynamics of the microemulsions used in the present work.

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