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Calorimetric investigation on the formation of palladium nanoparticles in water/AOT/*n*-heptane microemulsions

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Abstract

The formation enthalpy of palladium nanoparticles in water/sodium bis(2-ethylhexyl) sulfosuccinate (AOT)/*n*-heptane microemulsions as a function of the water/AOT molar ratio (R = [water]/[AOT]) was measured by a calorimetric technique. The results indicate that at $R < 10$ the energetic state of the palladium nanoparticles compartmentalized within the reversed AOT micelles is signficantly different from that in bulk water. Effects due to the small size of the palladium nanoparticles and to interactions between nanoparticles and the water/AOT interface are discussed.

Keywords: AOT; Heptane; Microemulsion; Nanoparticles; Palladium; Ternary system; Water

1. Introduction

Water–sodium bis(2-ethylhexyl) sulfosuccinate (AOT)–hydrocarbon microemulsions are thermodynamically stable systems constituted by nearly monodisperse water nanodroplets coated with a monolayer of oriented AOT molecules dispersed in the organic solvent. The radius (r_w) of the water nanodroplets, mainly regulated by the water to AOT molar ratio R (R = [water]/[AOT]), follows the simple equation [1]

$$r_w/\text{Å} = 1.8R \quad (1)$$

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Reversed micelles are also characterized by a wide variety of dynamical processes such as diffusion, shape fluctuations, intermicellar encounter and material exchange between neighboring micelles [2,3].

These well-established structural and dynamical properties of AOT reversed micelles suggest that water/AOT/hydrocarbon microemulsions are ideal media to synthesize solid nanoparticles by appropriate chemical reactions taking place inside the nanodroplets [4,5]. In fact, the material exchange process occurring on a millisecond timescale [6] allows hydrophilic reactants to come rapidly into contact and react. Moreover, the closed structure of AOT reversed micelles and their dispersion in a non-polar environment could prevent nuclei agglomeration and precipitation. Thus, by simply regulating the micellar radius, it could be possible to control the composition and size of solid nanoparticles. This is of great importance in order to obtain uniform catalysts with high surface/volume ratio [7-9].

Several techniques such as small-angle X-ray scattering, UV-vis spectrophotometry, transmission electron microscopy and light scattering [10] have been employed to investigate effectively the formation of metal colloids in microemulsions. In addition, we have previously shown that microcalorimetry is a sensitive technique to evidence the formation and eventually the growing process of nanoparticles [5,11]. Microcalorimetry is also expected to give interesting information on the energetic state of compartmentalized nanoparticles and on the influence of the micellar radius on the nanoparticle dimension [5].

Taking into account the usefulness of microcalorimetry and the importance of finely subdivided palladium as a catalyst for hydrogenation [12], we have performed a calorimetric investigation on the formation of Pd nanoparticles in water/AOT/*n*-heptane microemulsions. Palladium nanoparticles were obtained in situ by reducing potassium tetrachloropalladate with hydrazine sulfate. Because these reagents are hydrophilic, it must be anticipated that they are essentially located in the aqueous core of the AOT reversed micelles.

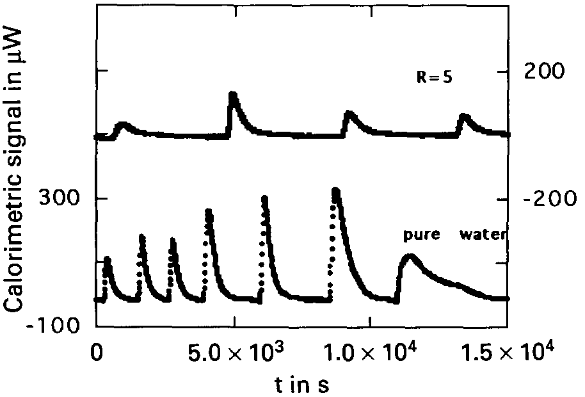

Fig. 1. Examples of calorimetric signal vs. time curves. Pure water, left scale; $R = 5$, right scale.

Table 1
Experimental molar enthalpy ($\Delta_{\mathrm{for}}H$, kJ mol^{-1}) for the formation of Pd nanoparticles in water/AOT/*n*-heptane microemulsions as a function of molar ratio S at various R values

S	$-\Delta_{\mathrm{for}}H$	S	$-\Delta_{\mathrm{for}}H$	S	$-\Delta_{\mathrm{for}}H$
$R = 1$		$R = 3$		$R = 4$	
0.114	61	0.476	90	0.123	150
0.171	43	0.715	123	0.431	181
0.286	53	1.00	110	0.739	202
0.400	50			1.00	235
0.571	57				
0.743	36				
1.00	29				
$R = 5$		$R = 8$		$R = 10$	
0.306	231	0.225	333	0.246	360
0.612	280	0.451	391	0.493	437
0.820	308	0.631	456	0.739	513
0.939	316	0.811	473		
$R = 15$		$R = 20$		Water	
0.233	341	0.232	337	0.053	300
0.467	442	0.464	463	0.106	349
0.700	500	0.743	489	0.160	361
1.00	546	1.00	560	0.266	359
				0.373	403
				0.532	479
				0.692	502

2. Experimental

2.1. Materials

Sodium bis(2-ethylhexyl) sulfosuccinate (AOT, Sigma, 99%), potassium tetrachloropalladate (K_2PdCl_4, Fluka, 32.5%, of Pd), hydrazine sulfate ($N_2H_4 \cdot H_2SO_4$, Fluka, >99%) and *n*-heptane (Merck, >99%) were used as received. All the solutions were prepared by weight.

2.2. Methods

Calorimetric measurements were performed at 25°C using a Thermal Activity Monitor (TAM) produced by LKB (LKB 2277) equipped with a mix-flow cylinder (LKB 2277-204) and a perfusion cell (LKB 2277-402). A typical run was carried out as follows. A known amount (about 1.5 g) of microemulsion, obtained by dissolving an appropriate amount of a 0.02 M aqueous solution of K_2PdCl_4 in an AOT/*n*-heptane solution at fixed AOT molar concentration ([AOT] = 0.33 M), was placed in the perfusion cell. This cell was inserted into the calorimeter and, after

Fig. 2. Electron micrograph of palladium nanoparticles from microemulsion at $R = 5$ (dimension of nanoparticles about 15 Å).

thermal equilibration, small amounts (10–50 μl) of a microemulsion obtained by dissolving in an AOT/*n*-heptane solution at [AOT] = 0.33 M an appropriate amount of a 0.16 M aqueous solution of $N_2H_4 \cdot H_2SO_4$, was added using an injection cannula connected to a Hamilton syringe. It must be pointed out that each experiment was carried out by mixing microemulsions with the same R in order to avoid any heat effect due to a change in the R value [13].

Two examples of calorimetric signal vs. time curves are shown in Fig. 1. The experimental enthalpies were obtained by integrating the area under the curves. The estimated uncertainty in the experimental enthalpies was ±0.2%. In Table 1, the experimental molar enthalpy ($\Delta_{\text{for}}H$) for the formation of Pd nanoparticles is reported as a function of the molar ratio $S = [N_2H_4 \cdot H_2SO_4]/[K_2PdCl_4]$.

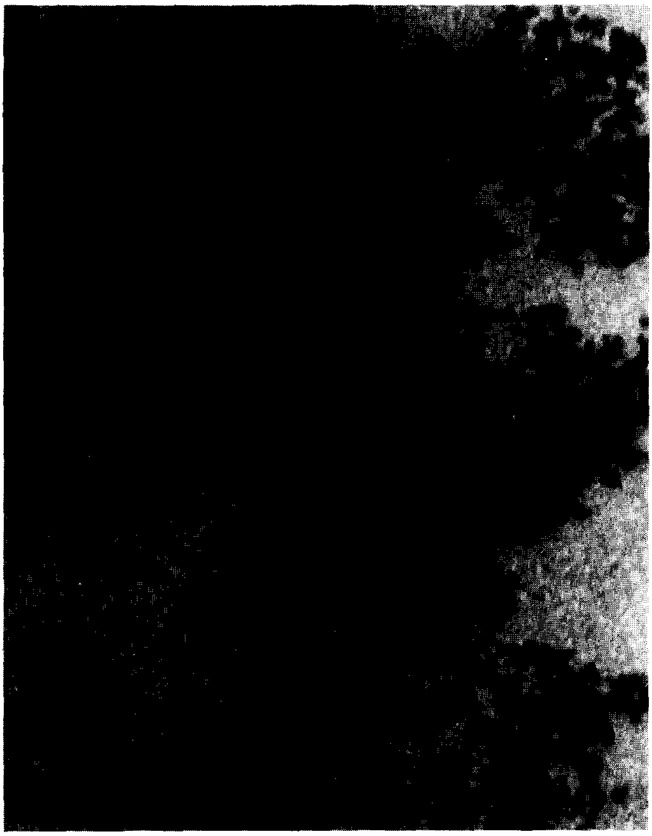

Fig. 3. Electron micrograph of palladium nanoparticles from microemulsion at $R = 8$ (dimension of nanoparticles about 30 Å).

It must be noted that the decay of the calorimetric signal after the maximum can be used to gain information on the growing rate of the particles for processes having a time constant τ greater than that of the microcalorimeter τ_s. In fact it is well known that after the initial nucleation, occurring on the timescale of a few seconds, the growth of nanoparticles occurs over a timescale of minutes or hours [14]. τ_s was obtained by analyzing the decay of the calibration signal. A τ_s value of 188 s was found (in the LKB application notes it is reported as 140–330 s).

At the end of each experiment, the samples were inspected visually. Only in the case of water and of microemulsions at $R > 8$ did part of the palladium form a thin precipitate. Microemulsions at $R < 10$ were stable for months without visible sedimentation.

In order to have direct experimental evidence on a nanometer scale, some samples were observed with a transmission electronic microscope (Philips, EM420). The solvent of the dilute sample (the surnatant in the case of microemulsions at

Fig. 4. Electron micrograph of palladium nanoparticles from surnatant of microemulsion at $R = 15$ (dimension of nanoparticles about 70 Å).

$R > 8$) containing nanocrystals was gently evaporated before inspection. It is interesting to note (see Figs. 2, 3 and 4) the absence of agglomeration after solvent evaporation. This indicates a repulsive mechanism active even when the particle concentration becomes high. Unfortunately, we were not able to evaluate the dimension of the Pd particles in the precipitate by electron microscopy.

3. Results and discussion

Fig. 5 shows the experimental molar enthalpies ($\Delta_{\mathrm{for}}H$) of formation of Pd nanoparticles as a function of $S = [N_2H_4 \cdot H_2SO_4]/[K_2PdCl_4]$ at various R values,

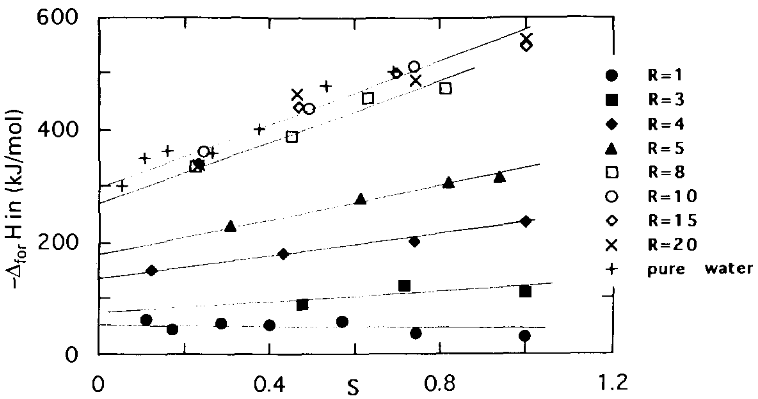

Fig. 5. Experimental molar enthalpies of formation $-\Delta_{for}H$ of Pd nanoparticles as a function of the ratio S at various R values.

together with the values in water. As can be seen, the enthalpies associated with Pd formation in water and in microemulsions at $R < 10$ are different. Because the $\Delta_{for}H$ values in water represent the heat accompanying the formation of Pd in spatially unconstrained conditions, it is reasonable to attribute the observed behavior in microemulsions to the compartmentalization effect, i.e. the formation of smaller particles and/or interactions between these particles and the water/surfactant interface. A perusal of Fig. 5 leads to the conclusion that

(a) at a given S value $\Delta_{for}H$ becomes more negative with increasing R;

(b) the trend observed in water is approached at $R > 8$;

(c) the slope of the linear plot of $\Delta_{for}H$ vs. S becomes more negative with increasing R.

In order to rationalize these results, it must be stressed that Pd atoms located at the surface of a nanoparticle are both a significant fraction of all the atoms present and they are present in a more highly energetic state. It follows that by decreasing the nanoparticle radius, their formation enthalpy is expected to increase and so become less negative. However, because decreasing R decreases the micellar radius and consequently smaller nanoparticles can be hosted in the aqueous core, the data can be taken as an indication that smaller nanoparticles are formed at lower R. This finding was directly confirmed by electron microscopy. Nanoparticles with a mean radius of 15, 30 and 70 Å were obtained in microemulsions at $R = 5$, 8 and 15, respectively. It is interesting to note that with Eq. (1) the micellar radius can be calculated and it is smaller than that of the nanoparticles ($r_w = 9$ Å at $R = 5$, $r_w = 14.4$ Å at $R = 8$, $r_w = 27$ Å at $R = 15$). Taking into account the dynamic character of the reversed micelles [2,15], the dimensions of the nanoparticles are evidently the result of a competition between the spontaneous tendency of particles to grow and the energetically unfavorable blowing up of the reversed micelles. The adsorption of the surfactant on the nanoparticles could have a role in their stabilization mechanism [16] as well as contributing to their formation enthalpy.

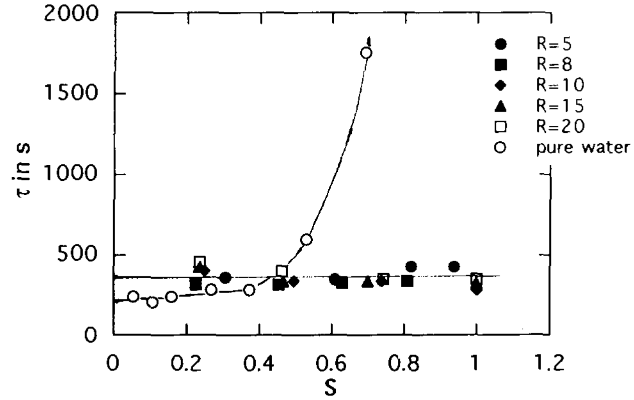

Fig. 6. Time constant τ as a function of S at various R values.

Our data and experimental evidence also indicate that the ability of the reversed micelles to stop the growth of nanoparticles is partially lost at $R > 8$.

With respect to point (c), it should be noted that an increase in S, i.e. further addition of reducing agent, can induce the formation of new nanoparticles and/or the growth of preexistent nuclei. Accordingly, the dependence of the $\Delta_{\mathrm{for}}H$ vs. S trends on R could be explained in terms of nanoparticle formation at a fixed radius at $R = 1$; whereas at $R > 1$, by increasing S, there is also a progressive increase in the nanoparticle radius. This increase should be more marked at higher R and in water.

In order to obtain information on the growth of the nanoparticles we have analyzed the decay of the calorimetric signal (see Fig. 1) using the equation [17,18]

$$P \propto \mathrm{e}^{-t/\tau} \qquad (2)$$

where P is the calorimetric signal, t the time, and τ is a time constant simply related to the rate constant (k) of the process ($\tau = 1/k$). Only for water and microemulsions at $R \geq 5$ was $\tau > \tau_s$ found. This indicates that at $R < 5$, the process is rapid, i.e. it is stopped at the nucleation stage [10]. In Fig. 6 the τ values are shown as a function of S for microemulsions at $R \geq 5$. As can be seen, the behavior in water is different from that observed in microemulsions. In water, the absence of spatial constraints involves an initial rapid formation and growth of Pd particles. Increasing S leads to a dramatic decrease in the rate process probably due to the occurrence of a slow agglomeration of Pd particles. In contrast, in microemulsions the process is always quite rapid. This could be taken as an indication that in these systems agglomeration is absent. If this is true, it seems reasonable to hypothesize that the thin precipitate observed at $R > 8$ is made up of fractal clusters of Pd nanoparticles similar to that shown in Fig. 4.

Acknowledgments

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References

[1] J. Eastoe, G. Fragneto, B.H. Robinson, T.F. Towey, R.K. Heenan and F.J. Leng, J. Chem. Soc. Faraday Trans. 1, 88 (1992) 461.

[2] P.D.I. Fletcher and B.H. Robinson, Ber. Bunsenges Phys. Chem., 85 (1981) 863.

[3] G. D'Arrigo, A. Paparelli, A. D'Aprano, I.D. Donato, M. Goffredi and V. Turco Liveri, J. Phys. Chem., 93 (1989) 8367.

[4] J.H. Fendler, Chem. Rev., 87 (1987) 877.

[5] A. D'Aprano, F. Pinio and V. Turco Liveri, J. Solution Chem., 20 (1991) 301.

[6] P.D.I. Fletcher, A.M. Howe and B.H. Robinson, J. Chem. Soc. Faraday Trans. 1, 83 (1987) 985.

[7] Y.M. Tricot and J. Fendler, J. Phys. Chem., 90 (1986) 3369.

[8] F. Lichterfeld, T. Schmeling and R. Strey, J. Phys. Chem., 90 (1986) 5762.

[9] C. Petit, P. Lixon and M.P. Pileni, J. Phys. Chem., 94 (1990) 1598.

[10] M.A. Lopez-Quintela and J. Rivas, J. Coll. Interf. Sci., 158 (1993) 446.

[11] V. Arcoleo, M. Goffredi and V. Turco Liveri, Thermochim. Acta, 233 (1994) 187.

[12] M. Boutonnet, J. Kizling, V. Mintsa-Eya, A. Choplin, R. Touroude, G. Maire and P. Stenius, J. Catal., 103 (1987) 95.

[13] A. D'Aprano, A. Lizzo and V. Turco Liveri, J. Phys. Chem., 91 (1987) 4749.

[14] J.H. Clint, I.R. Collins, J.A. Williams, B.H. Robinson, T.F. Towey, P. Cajen and A. Khan-Lodhi, Faraday Discuss., 95 (1993) 219.

[15] H.F. Eicke and P.E. Zinsli, J. Coll. Inter. Sci., 65 (1978) 131.

[16] M. Boutonnet, J. Kizling, P. Stenius and G. Maire, Coll. Surf., 5 (1982) 209.

[17] A. Buzzell and J.M. Sturtevant, J. Am. Chem. Soc., 73 (1951) 2454.

[18] C.H. Lueck, L.F. Beste and H.K. Hall, J. Am. Chem. Soc., 67 (1963) 972.