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Physico-chemical investigation of nanostructures in liquid phases: Nickel chloride ionic clusters confined in sodium bis(2-ethylhexyl) sulfosuccinate reverse micelles

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ABSTRACT

The confinement of finite amounts of nickel chloride in the hydrophilic core of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) reverse micelles dispersed in n-heptane has been investigated by FT-IR, UV–vis-NIR and fluorescence spectroscopies. The analysis of experimental data consistently leads to hypothesize that $NiCl_2$ forms small size ionic clusters stabilized by a monolayer of oriented surfactant molecules. Due to confinement and interfacial effects, these ionic clusters show peculiar photophysical properties, which are different from those possessed by the bulk material. From $NiCl_2$/AOT/*n*-heptane solutions, by evaporation of the organic solvent, interesting salt/surfactant nanocomposites at various salt concentrations have been prepared and characterised by WAXS. On the other hand, after mix with Na_2S-containing dry micellar systems, the formation of NiS nanoparticles have been ascertained by UV–vis spectroscopy.

1. Introduction

Micellar solutions have proven to be very efficient compartmentalizing systems for the chemical synthesis of nanoparticles. In particular w/o microemulsions have been employed for decades in the preparation of nanocrystals of a wide range of substances: noble metals, metal sulfides, etc. [1–6].

In these systems, the presence of water nanodroplets stabilised by a layer of opportunely oriented surfactant molecules bestows a particular capability of solubilising hydrophilic substances encapsulating them in the hydrophilic micellar core. At the same time, thanks to their peculiar structure, reverse micelles behave as real confining hydrophilic nanoreactors. The dynamical features of these supramolecular aggregates, on the other hand, confer them a particular fluidity and permit an intermicellar exchange of materials usually occurring in the timescale of milliseconds [7].

So, generally, nanoparticle synthesis was performed by mixing two w/o microemulsions containing, respectively, two different hydrophilic reagents confined in the micellar cores. The intermicellar exchange of material allows the two reagents to come into contact and react inside the hydrophilic micellar domain while the close structure of the surfactant layer confines the resulting products. The subsequent adsorption of surfactant molecules stabilizes the products hindering the thermodynamic trend to their unlimited growth. For example, starting from a microemulsion containing a metal salt, metal nanoparticles can be prepared by mix with another microemulsion containing an opportune reducing agent, whereas nanoparticles of water-insoluble salt can be prepared by mix with another salt-containing microemulsion carrying the opportune counter-anion [8,9]. The amount of water, influencing both the micellar structure and dynamics (specifically micellar size and intermicellar exchange rate) can be used to tune the final nanoparticle size, thus allowing a quite fine size control and making this synthetic way efficient and versatile [10].

However, the presence of water itself precludes the preparation of nanoparticles of water-soluble materials. This limitation has been overcome by the use of dry micellar systems obtained by vacuum-drying salt-containing w/o microemulsions with the formation of salt/surfactant nanocomposites and resuspending them with organic solvent [11].

In this process, the evaporation of volatile components of a w/o microemulsion implies a progressive subtraction of water from the hydrophilic micellar nanodomain allowing the precipitation of the hydrosoluble salt within the micellar core in a sort of "confined crystallisation". Not only this procedure allowed the synthesis of water-soluble nanoparticles, but also opened the way to a wide class of novel nanomaterials. In fact, in analogy with what was done with salt-containing w/o microemulsions, it is possible to mix two dry micellar systems carrying nanoparticles of two different water-soluble materials. In this case, nanoparticles of two different materials can react in the hydrophilic domain of the micellar core in a sort of solid–solid reaction between nanoparticles in the confined space of reverse micelles [12,13].

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In such conditions, the absence of water has a two fold effect: first, it makes reverse micelles smaller than water-containing ones thus giving very small nanoparticles with consequently marked quantum size effects and, secondly, it enhances the surfactant adsorption to nanoparticle surface thus hindering the subsequent nanoparticle growth. Furthermore, it can be expected that the peculiar reaction path confers to the resulting products novel structural and chemico-physical characteristics.

In this approach it is of utmost importance the preparation of the solutions containing water-soluble nanoparticles because they must be stable enough to be prepared and manipulated before their mix, but, at the same time, reactive enough to allow the successive nanoparticle–nanoparticle solid state reaction through their mix.

The focus of this article is to prepare and characterize $NiCl_2$-containing dry micellar systems to be used as precursors in the synthesis of NiS Q-dots through mix with Na_2S nanoparticle-containing dry micellar solutions. This specific application comes from the consideration that very little is known about NiS Q-dots, even though they represent a very interesting and promising material (it is a very small bandgap semiconductor, a paramagnetic–antiferromagnetic (PM–AFM) phase-changing material and it is used in hydrodesulfurisation catalysis and solar storage) [14].

In our opinion, this lack of knowledge is mostly due to the difficulties encountered so far in their synthesis, because the classical method of mixing two water-containing reverse micellar systems (containing Ni^{2+} and sulfide salt, respectively) is unsuccessful since it involves uncontrollable nanoparticle growth and massive precipitation. As a consequence only few and complex methods for their preparation are reported so far [15].

Moreover, from a theoretical prospect, this contribution aims to shed some light on the microscopic processes involved in the entrapment of hydrophilic substances in dry micellar cores and controlling the nanoparticle–nanoparticle reaction in such peculiar systems.

2. Experimental

2.1. Materials

Sodium bis(2-ethylhexyl)sulfosuccinate (aerosol-OT, AOT, Sigma 99%) was stored in a desiccator and used after at least 1 week.

n-Heptane (Carlo Erba Reagenti purum RE 98+%), nickel chloride hexahydrate (Carlo Erba AnalytiCals RPE 99+%) and sodium sulfide nonahydrate (Sigma ⩾98%, ACS Reagent) were used as received.

Bidistilled water was used in all experiments.

2.2. Methods

All samples were prepared by weight. Water/AOT/n-heptane microemulsions were obtained by adding the appropriate amount of 0.2 mol kg^{-1} AOT/*n*-heptane solution to a weighted amount of water to give the desired water-to-AOT molar ratio ($R_w = [water]/[AOT]$). Similarly, each salt-containing w/o microemulsion was prepared by adding the appropriate amount of w/o microemulsion to a weighted amount of $NiCl_2{\cdot}6H_2O$ in order to obtain the desired salt-to-AOT molar ratio ($R_s = [NiCl_2{\cdot}6H_2O]/[AOT]$). Solubilisation of the salt in w/o microemulsion was sped up by ultrasonication.

The salt solubility at each R_w was determined by visual inspection of samples prepared at various R_s values.

The subsequent preparation of each salt-surfactant composite was carried out by placing about 3 g of salt-containing w/o microemulsion at fixed R_w ($R_w = 4$) and at the desired R_s value in a glass Petri dish (diameter about 10 cm) and keeping it in a desiccator connected to a rotative pump allowing a vacuum of 10^{-2} mbar (KNF Neuberger Laboport). Even if volatile components of samples at a visual inspection appeared absent after a couple of hours, all salt-surfactant composites were kept under vacuum for one more day. The constant value of pressure (about 10^{-2} mbar) reached after this time suggested that the evaporation of volatile components was complete. Finally, the salt-surfactant composites were resuspended in the appropriate amount of *n*-heptane to restore the original AOT concentration. The quantitative determination of the amount of water in AOT/n-heptane solution (resuspension at $R_s = 0$) was performed by measuring the OH stretching band area and comparing it with that of water/AOT/n-heptane microemulsions prepared by adding known amounts of water. FT-IR spectra were recorded in the 5000–400 cm^{-1} range with a Perkin Elmer Spectrum GX FT-IR System through a cell equipped with KBr windows. Each sample was examined for 10 scans at a spectral resolution of 1 cm^{-1}.

UV–vis spectra were recorded in the range 300–1000 nm with a Perkin Elmer (Lambda 20) UV–vis spectrometer using quartz cuvettes.

Steady-state fluorescence measurements were made using a Horiba Jobin Yvon spectrofluorimeter (Fluoromax-4) arranged in T-shaped geometry.

X-ray powder diffraction spectra of composites were recorded by a Philips diffractometer (PW1050/39 X Change) equipped with a copper anode (Cu Kα, 1.5418 Å).

All measurements have been carried out in thermostatted compartments at 25 °C.

3. Results and discussion

The maximum amount of $NiCl_2{\cdot}6H_2O$ that can be dissolved in water/AOT/n-heptane to give clear and stable salt-containing microemulsion expressed as salt-to-AOT molar ratio ($R_{s,max}$) has turned out to be 0.16 ± 0.01 in w/o microemulsion at water-to-AOT molar ratio (R_w) $R_w = 4$. In this system the maximum value of solubility occurs as a delicate balance of two opposing factors:

(i) the solubilising action of water that leads to an increase of solubility with the R_w value, since the amount of salt that can be dissolved in bare AOT/*n*-heptane solution ($R_w = 0$) is exiguous;
(ii) the salt effect on the water solubility in microemulsions, since at higher R_w ($R_w \geqslant 4$) values a salt-rich aqueous solution separates from the microemulsion.

The $R_{s,max}$ values found at various R_w are reported in Table 1.

The subsequent evaporation of the volatile components (water and *n*-heptane) of these salt-containing w/o microemulsions allows the formation of salt-surfactant composites that can be resuspended in organic solvent. However, we have found that clear resuspensions can be obtained only for R_s values lower than 0.10. This is due to the fact that in the evaporation process the progressive subtraction of water from the micellar cores strongly depresses the salt solubility and makes it possible the formation of NaCl nuclei originated by the metathesis reaction between AOT

Table 1
$R_{s,max}$ values at various R_w.

R_w	$R_{s,max}$
0	$<10^{-3}$
2	0.14
4	0.16
9	<0.10