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SHORT COMMUNICATION

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# A simple method to prepare solid nanoparticles of water-soluble salts using water-in-oil microemulsions

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**Abstract** A new and simple method to prepare solid nanoparticles of water-soluble salts using water-in-oil microemulsions is described. In particular, starting from water/sodium bis(2-ethylhexyl)sulfosuccinate/*n*-heptane microemulsions carrying inside the aqueous core of the reversed micelles some water-soluble salts [$CaCl_2$, $Na_2HPO_4$, $Cu(NO_3)_2$], after evaporation of the volatile components (water and apolar organic solvent), the resulting inorganic salt/surfactant composites were found to be totally dispersible in pure *n*-heptane. The presence of nanoparticles in these resuspended composites was ascertained by transmission electron microscopy observation of samples obtained by gentle evaporation of the organic solvent.

**Key words** Water-soluble inorganic salts · Nanoparticles · Water-in-oil microemulsions

## Introduction

Among the various physical and chemical methods employed to obtain nanoparticles, it has recently been shown that an interesting and promising one is based on the use of water-in-oil (w/o) microemulsions as reaction and solvent media since they easily allow both the synthesis and stabilization of water-insoluble salts [1–3]. In fact, by mixing two w/o microemulsions carrying inside the aqueous core of the reversed micelles the appropriate ions, as a consequence of micellar diffusion and of the fast intermicellar exchange process, these species come rapidly in contact and react, whereas the closed structure of the micelles, their dispersion in a nonpolar environment and surfactant adsorption on the nanoparticle surface could inhibit their unlimited growth, allowing fine size control [4–6].

In the ambit of our research in this field, we have recently found that it is also possible to obtain nanoparticles of water-soluble salts using w/o microemulsions. In particular, starting from water/sodium bis(2-ethylhexyl) sulfosuccinate (AOT)/*n*-heptane microemulsions carrying inside the aqueous core of the reversed micelles a water-soluble salt, after evaporation of the volatile components (water and apolar organic solvent) and resuspension of the salt/surfactant composite in a dry organic solvent, nanoparticles of the salt can be found in the liquid phase. This was ascertained by transmission electron microscopy (TEM) observation of samples obtained by gentle evaporation of the organic solvent. Incidentally, it must be noted that the existence of nanoparticles in these samples also allows the possibility to prepare solid nanocomposites composed of nanoparticles of water-soluble salts dispersed in a matrix of surfactant. It must also be pointed out that the above procedure for the preparation of solid nanoparticles of water-soluble compounds can be considered as an alternative to that reported by Delfort et al. [7], where nanoparticles of inorganic chemical species are synthesised by a one-step process which allows both the synthesis of the inorganic chemical species and the surfactant micellization.

In this preliminary report, the preparation procedure of nanoparticles of some water-soluble salts [$CaCl_2$,

$Na_2HPO_4$, $Cu(NO_3)_2$] by water/AOT/*n*-heptane w/o microemulsions and their structural characterization by TEM are presented.

## Materials and methods

AOT (Sigma, 99%), calcium chloride dihydrate (Carlo Erba, 99%), sodium phosphate (dibasic anhydrous, Sigma, 99%), copper (II) nitrate hemipentahydrate (Aldrich, 98%) and *n*-heptane (Sigma, 99%) were used as received.

All the samples were prepared by weight. Microemulsions were prepared by adding to a 0.15 *m* AOT/*n*-heptane solution the appropriate amount of a 0.1 *m* aqueous solution of the salt [$CaCl_2$, $Na_2HPO_4$, $Cu(NO_3)_2$] in order to obtain a stable and monophasic liquid system at $R = 10$ ($R$ = [water]/[AOT]). After complete solubilization of the aqueous solution, the volatile components (water and organic solvent) of these w/o microemulsions were evaporated in vacuum and the resulting salt/surfactant composites were stored under high vacuum for several days. Finally these dry composites were fully dispersed in pure *n*-heptane. Samples for TEM (Jeol 1220 T operating at 120 kV) were prepared by placing a drop of these solutions on a carbon–copper grid and allowing the organic solvent to evaporate at room temperature.

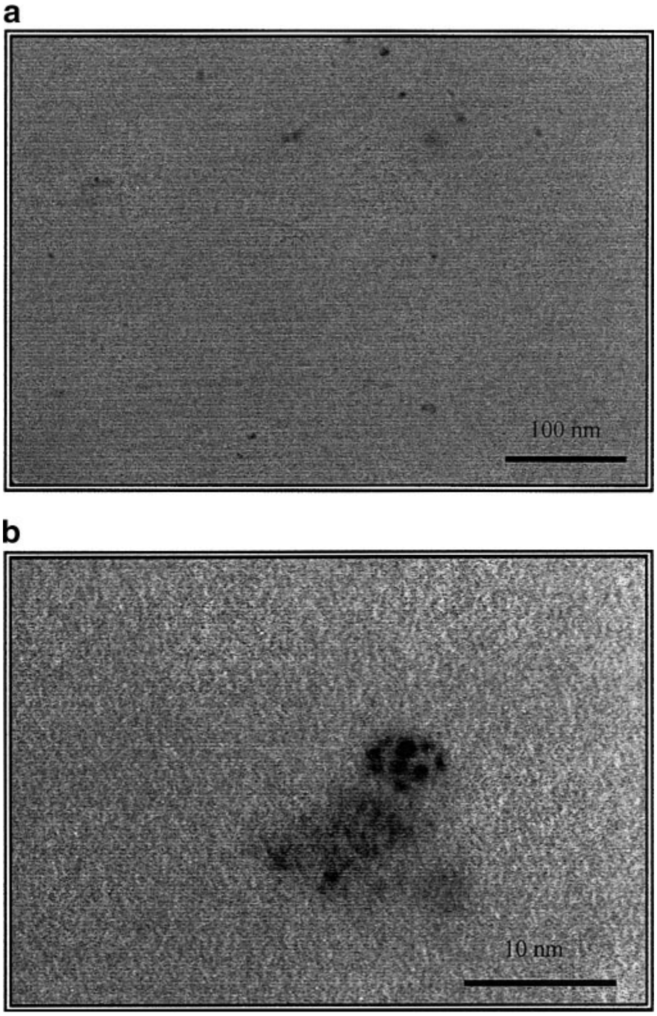

**Fig. 1** **a** Electron micrograph of $Cu(NO_3)_2$ nanoparticles (5 nm < $d$ < 15 nm) dispersed in a sodium bis(2-ethylhexyl) sulfosuccinate (AOT) matrix [sample obtained from an aqueous solution of $Cu(NO_3)_2$/AOT/*n*-heptane microemulsion at $R$ = 10, magnification ×14 4000]. **b** Electron micrograph of an aggregate of $Cu(NO_3)_2$ nanoparticles (1 nm < $d$< 2 nm) dispersed in an AOT matrix [sample obtained from an aqueous solution of $Cu(NO_3)_2$/AOT/*n*-heptane microemulsion at $R$ = 10, magnification ×240 0000]

## Results and discussion

Some representative electron micrographs of samples obtained from the resuspended salt/surfactant composites are shown in Figs. 1–3. A perusal of these figures shows the presence of nanoparticles in all the samples investigated with sizes ($d$) ranging from 1 to 25 nm. In the micrographs at low magnification, the nanoparticles appear to be statistically distributed in the samples; however, in those at high magnification, it was frequently observed that each nanoparticle is actually a cluster of smaller nanoparticles with sizes ranging from 1 to 2 nm.

Since the radius of the micellar core ($r$) of AOT reversed micelles is regulated by the molar ratio, $R$, according to the equation [8]

$$r(\mathrm{nm}) = 0.18R \tag{1}$$

it is worth noting that, in our experimental conditions, $r$ = 1.8 nm and the mean number of ions of the water-soluble salts for each micelle is about 2.2. This suggests that during the evaporation of the volatile components of the microemulsions (water and *n*-heptane), in addition to the progressive increase of the micellar concentration and decrease of the micellar radius, many intermicellar exchanges occur, enabling the formation

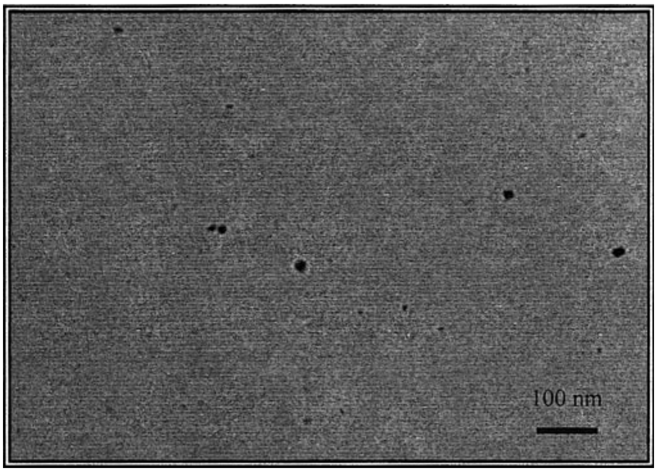

**Fig. 2** Electron micrograph of $CaCl_2$ nanoparticles (8 nm < $d$ < 25 nm) dispersed in an AOT matrix [sample obtained from an aqueous solution of $CaCl_2$/AOT/*n*-heptane microemulsion at $R$ = 10, magnification ×12 0000]

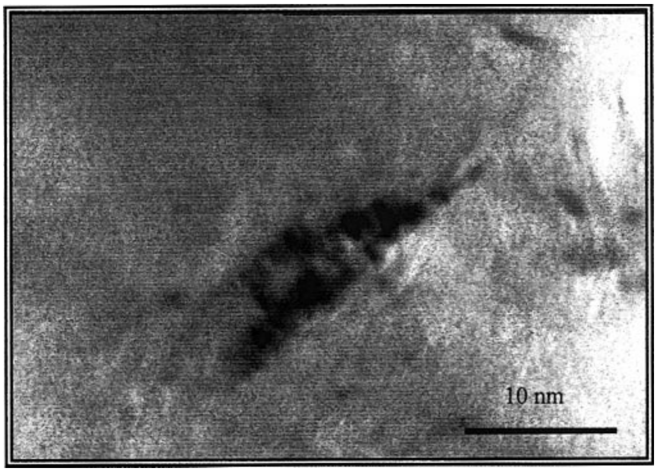

**Fig. 3** Electron micrograph of an aggregate of $Na_2HPO_4$ nanoparticles (1.5 nm $<$ $d$ $<$ 2 nm) dispersed in an AOT matrix [sample obtained from an aqueous solution of $Na_2HPO_4$/AOT/*n*-heptane microemulsion at $R = 10$, magnification ×300 0000]

of nanoparticles with sizes in the range 1–25 nm ($10^3$–$10^7$ atoms). This observation underlines the importance of the evaporation rate on the control of the nanoparticle size. Moreover, the observed tendency to form nanoparticle aggregates reveals the existence of two counteracting effects, i.e., a short-range attractive interparticle interaction and a mechanism able to inhibit nanoparticle coalescence attributable most probably to surfactant adsorption on the nanoparticle surface. Obviously, the control of other parameters (nature of surfactant, micellar size, salt concentration, etc.) able to influence both these processes could allow a finer size control.

In conclusion, our finding opens the door for the preparation and stabilization of nanoparticles of a wide class of water-soluble solid substances and potentially for the production of new technologically interesting materials. We are now actively carrying out experiments on selected compounds in order to find the specific conditions which allow the best nanoparticle size control and we aim to elucidate the microscopic processes involved in their formation and arrested growth.

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