



Attempts to control depletion in the surfactant-assisted stabilization of single-walled carbon nanotubes



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HIGHLIGHTS

- The stability of dispersions containing single-walled carbon nanotubes was investigated.
- Depletion phenomena occur at moderate surfactant content.
- Stabilization is controlled by added electrolytes.
- Surfactant mixtures are effective in the stabilization.
- The quality of surface coverage is relevant for an effective stabilization.

GRAPHICAL ABSTRACT



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ABSTRACT

Single-walled carbon nanotubes were stabilized by an anionic surfactant, sometimes in mixture with a nonionic one (Triton TX-100), and/or in presence of salt. The stabilizing activity of sodium dodecylsulfate is poor, with occurrence of phase separation at moderate surfactant content; even lower is the one ascribed to TX-100. We quantified the stabilization in terms of surface coverage by the adsorbing species; the effect is counteracted by the presence of micelles present in the surrounding medium. A chemical approach accounted for the competition between surface adsorption and micelle formation.

Destabilization of the dispersions is due to unbalanced osmotic effects and is related to depletion. The above phenomenon occurs when the volume fraction of micellar aggregates reaches a certain threshold, whose value is related to micelle size. Depletion was avoided by selecting the maximum possible amounts of sodium dodecylsulfate, NaCl and/or Triton TX-100. In mixed systems the stabilization is active for longer times compared to dodecylsulfate, although depletion occurs at lower surfactant content.

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1. Introduction

Materials having sizes at the nano-scale level are relevant in many technologically-oriented applications [1–5]. Since the forecasts by Richard Feynman [6], the number of pertinent papers has significantly increased. Many aspects of nano-materials are well known, others require further characterization work. Carbon nanotubes, CNTs, deserve special attention, because of their outstanding electronic, thermo-conductive, and mechanical properties [7–12].

They are poorly dispersible and form bundles in most polar liquids. Such a drawback hinders practical applications. To avoid bundling, due to van der Waals and π - π interactions between CNTs, stabilization is required.

We do not consider covalent stabilization [13], and focus on the adsorption-based one [14–17]. Adsorption-based stabilization hinders the formation of flocs, gels and nematic phases made of CNTs. Surfactants are possible stabilizers; polymers are used too, sometimes in combination with surface active agents. On this line, the phase diagrams of polymer-CNT, and surfactant-CNT systems were investigated and the existence of “stable” dispersions was inferred [18–20].

To avoid phase separation of CNT colloids, the following requirements must be fulfilled:

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- a) significant surface adsorption energy of the dispersants and formation of layers that prevent other particles coming closer than distances required for interactions to occur; and,
- b) high depletion thresholds.

The aforementioned effects are in competition each with the other. It is required, therefore, to look for dispersion strategies based on a delicate balance among such competing effects. A refined formulation work is required and a deep knowledge of all forces in action. Adsorption may be improved by selecting appropriate surfactants, keeping in mind that their efficiency is tuned by adding polymers, co-surfactants and/or salts.

In this contribution, we experienced if protocols based on surfactant content and nature, use of blends, and added salt improve the dispersion stability and reduce depletion. The latter is a crucial problem in formulation, since unbalanced osmotic effects always take place in dispersions of colloid particles, with subsequent depletion. Dilute systems were screened in conditions that do not allow percolation and/or the formation of gels at low CNT content [20,21].

The effects that surfactants and/or electrolytes play on dispersions made of single-walled carbon nanotubes, SWCNTs, was investigated. The reasons for using SWCNTs in place of multi-walled ones arise by the fact that the size dispersity solely refers to the distribution in length.

The present results may improve the quality of the procedures requiring surfactant-assisted nanotube stabilization. In perspective, they are promising in technological applications, for instance in the preparation of typewriting fluids [22], or surface coatings.

2. Experimental

2.1. Materials

2.1.1. Chemicals

SWCNTs were from Unydim, Houston (TX), lot. P0355. The nominal purity indicated by the purveyor is $\approx 98\%$. SWCNTs have low dispersity in diameters, D . In 1.00 sodium dodecylsulfate wt% ($=0.035 \text{ mol kg}^{-1}$), for instance, a TEM-based distribution function for SWCNTs indicates constancy in D ($2.0 \pm 1.0 \text{ nm}$) and tiny amounts of bundles. According to TEM, conversely, their length, L , spans from 300 nm to over $1 \mu\text{m}$ [23]. The average length inferred by a statistical distribution function is $700 \pm 150 \text{ nm}$.

Sodium dodecylsulfate, SDS, Sigma Aldrich, was dissolved in hot ethanol, filtered, precipitated by cold acetone, and vacuum dried at 70°C . Its purity was checked by conductivity and surface tension. The critical micellar concentration of SDS, CMC, is close to previous data [24]. Sodium octylsulfate, SOS, and sodium p-dodecylbenzenesulfonate, SDBzSu, Sigma, were purified by the same procedures, and controlled as before. Triton TX-100, Sigma, an alkylphenol with ≈ 10 oxyethylene units per molecule, was used as such. It was tested by surface tension and CMC (about 0.06 wt\% , i.e. $2 \times 10^{-4} \text{ mol kg}^{-1}$ at 25.0°C).

NaCl, Sigma, was dried in vacuum at 150°C , and used as such. Water was doubly-distilled over KMnO_4 and bubbled by N_2 , to reduce the presence of CO_2 . Its ionic conductance, χ , is $< 1 \times 10^{-7} \Omega^{-1} \text{ cm}^{-1}$, at 25.00°C .

2.1.2. Material preparation

SWCNTs were dried, reduced in powder, recovered, dispersed in 1.0 wt\% SDS, and sonicated by an INOVA unit at 40°C for some hours, at 20 kHz and 200 W . Sonication and/or stirring continued until constancy in optical absorbance was detected. Centrifugation ensures a complete SWCNT recovery. The above procedures were repeated three times. 1.00 wt\% SDS stabilizes up to 2.0 g kg^{-1} of

SWCNTs. The effective SWCNT concentration in SDS dispersions was controlled by optical absorbance at 660 nm and 25.0°C . The absorbance was inferred according to previous indications by Regev et al. [25].

Because of the significant color intensity of concentrated dispersions, we focused on mixtures containing 1.0 g kg^{-1} of SWCNTs. More SDS was added to the mixtures, eventually in presence of $0.050 \text{ mol kg}^{-1}$ NaCl. TX-100 was directly added to SDS-containing dispersions; in pure form, in fact, it is a much less efficient dispersant than SDS. The dispersing capacity of SOS and SDBzSu is much lower than those pertinent to both SDS and TX-100, and is not reported.

2.2. Methods

2.2.1. Dynamic light scattering

A Malvern Zeta Nanosizer worked at $25.0 \pm 0.1^\circ\text{C}$. The unit is equipped with a 632.8 nm laser source, working in back-scattering mode, at 173° . This configuration minimizes the drawbacks due to the turbidity and dark color intensity of the dispersions. Correlation decays gave the Z-average hydrodynamic diameters, $2R_H$, and the size polydispersity index, PdI .

2.2.2. Electro-phoretic mobility

Measurements were run by a Malvern laser-Doppler facility, working between -150 and $+150 \text{ mV}$. Cells consist of U-shaped tubes with 3.0 mm inner diameter in which gold-coated electrodes are fitted. The temperature is controlled by a Peltier unit at $25.0 \pm 0.1^\circ\text{C}$. The radiation diffused from particles moving under an applied electric field, \vec{E} , is shifted compared to static conditions. The phase is compared to that without \vec{E} and elaborated. More details on the measuring procedures are reported elsewhere [26].

2.2.3. TEM microscopy

TEM was run by a ZEISS EM 900 electron microscope at an acceleration voltage of 80 kV . Drops of the dispersion were stratified on carbon-covered copper grids, and allowed to adhere. Solvent in excess was removed by filter paper. Thereafter, 2.00 wt\% phosphotungstic acid was added. The samples were dried by N_2 gas flow before measurements. Details on the measuring procedures are given elsewhere [27].

2.2.4. UV-vis methods

A Unicam double beam spectrophotometer performed the measurements at $25.0 \pm 0.1^\circ\text{C}$, after sonication. Absorbance, A (in a.u.), decreases with λ , Fig. 1. A values are moderate, because of the low amount of SWCNTs, and decrease with aging, if the dispersions are not properly stabilized. When estimates of SWCNT content are required, absorbance was measured at 660 nm . The related accuracy is to $\pm 3\%$ [25].

2.2.5. Optical microscopy

The dispersions were investigated at 25.0°C by a CETI optical microscope, working in white or polarized light. The microscope is equipped with a Linkam TP 96 thermostatic unit, ensuring the constancy in temperature to 0.1°C . When required, a camera was fitted in the microscope head and the resulting photos were imaged. To avoid drawbacks due to the significant color intensity of the dispersions, 0.1 mm thin Teflon spacers were used. The presence of precipitates was inferred, but no flocs or nematic order were detected.

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