

# Carbon Nanotube Dispersion : Science or Art?

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## ABSTRACT

We have developed a series of strategies to unravel the mechanism of adsorption of surfactants and polymeric dispersants onto single wall and multi wall carbon nanotubes. Using these guidelines, we have prepared a novel series of polymeric surfactants that very strongly adsorb onto the nanotube surface, using a controlled radical RAFT polymerization process. They allow to disperse single wall and multi wall nanotubes in either organic solvents (isooctane, THF) or in water even at high concentration of carbon nanotubes ( $c = 50 \text{ g.L}^{-1}$  or higher). For each set of dispersion experiments, Langmuir absorption isotherms have been established by varying temperature and the nature of electrolytes. Dispersion have also been studied by Raman spectroscopy (RBM bands), AFM, TEM microscopy and broadband dielectric spectroscopy. This study has allowed us to elaborate a strategy for successful dispersion of nanotubes followed by their encapsulation in a variety of polymers.

**Keywords:** carbon nanotube, dispersion, aggregation, polymer, surfactant

## 1 INTRODUCTION

Since the landmark paper by Iijima [1], carbon nanotubes (CNTs) have attracted tremendous attention due to their unique mechanical, electrical and thermal properties [2]. However, the utilization of CNTs has been hampered by their poor solubility in any solvent, as well as their tendency to aggregate. In order to break apart these aggregates [3], a mechanical device such as a sonicator or a microfluidizer needs to be used to overcome the van der Waals forces which hold the CNT bundles together. However, if no stabilizing molecule is present in the solution, the CNTs will aggregate very rapidly. In this communication, we present salient results on the dispersion of CNTs by common surfactants in water, as well as by polymeric surfactants either in water or in organic solvents. Importantly, the dispersion involves no covalent modification of the CNT.

## 2 RESULTS AND DISCUSSION

We recently reported the adsorption isotherms of four different surfactants, sodium dodecyl sulfate (SDS), sodium dodecyl benzyl sulfonate (SDBS), benzethonium chloride

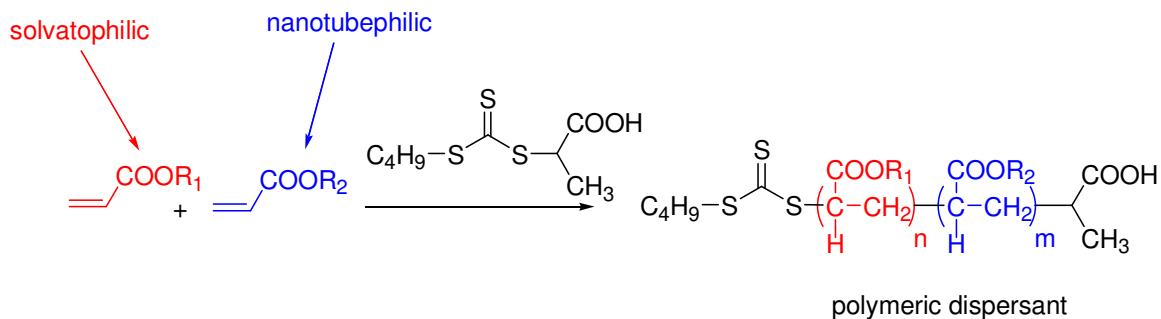
(BzT) and Triton X-100 on multi-wall carbon nanotubes (MWCT) and single-wall (SWCT) in water [4]. It was found that the enthalpy of adsorption is primarily influenced by the length of the hydrophobic tail, but much less influenced by the nature of the polar head. In an adsorption isotherm, one measures the amount of adsorbed dispersant (or surfactant) vs the amount of free dispersant,  $C_{\text{free}}$ , in the solvent. When the total surfactant concentration is kept below cmc, adsorption of surfactant unimers shows a Langmuir-type behavior, as expressed by

$$\Gamma = \frac{\Gamma_s c_{\text{free}}}{a + c_{\text{free}}} \quad (1)$$

where  $\Gamma$  is the surface coverage of surfactant, in  $\text{mol/m}^2$ ,  $\Gamma_s$  is the saturation coverage, which corresponds to the value of  $\Gamma$  when a continuous monolayer of unimers is adsorbed at the surface and  $a$  is the desorption equilibrium constant (unit mol/L) which also corresponds to the surfactant concentration necessary to cover 50% of the surface. The purity of the CNTs was found to be a key element in the outcome of the dispersion. Indeed, CNTs are contaminated by metal impurities. In water, these metallic impurities are in part dissociated under the form of metallic cations, the amount of which depends on the pH and ionic strength of water as well as on the past history of the CNT (contact with reducing, oxidizing or acidic compounds). Thus, the metallic impurities play an important role when the CNT is dispersed with a negatively charged dispersant such as SDS and SDBS. On the contrary, with non-ionic and cationic surfactants such as Triton X100 and BzT, we found that the metallic impurities had little influence on the outcome of the dispersion.

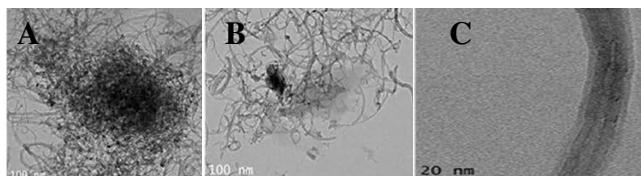
Compound	Type / Conditions	a mmol/L	$\Gamma_s$ $\mu\text{mol/L}$
<b>Surfactant</b>			
SDS	MWNT / H <sub>2</sub> O	0.13	2.20
<b>Polymer</b>			
(AA) <sub>4</sub> (BA) <sub>10</sub>	MWNT / H <sub>2</sub> O	0.23	10.1
(EHA) <sub>6</sub> (CEM) <sub>17</sub>	MWNT /isooctane	0.15	0.23
(EHA) <sub>6</sub> (CEM) <sub>17</sub>	MWNT /toluene	0.95	0.24
(EHA) <sub>12</sub> (CEM) <sub>4</sub>	MWNT /isooctane	0.20	0.40
(EHA) <sub>12</sub> (CEM) <sub>4</sub>	SWNT/isooctane	0.50	0.36

Table 1: Summary of the adsorption isotherms.



**Figure 1.** Preparation of polymeric dispersants specific for nanotubes – For dispersion in water  $R_1 = H$  (AA) and  $R_2 = C_4H_9$  (BA), whereas for dispersion in isoctane,  $R_1 = EHA$  and  $R_2 = CEM$

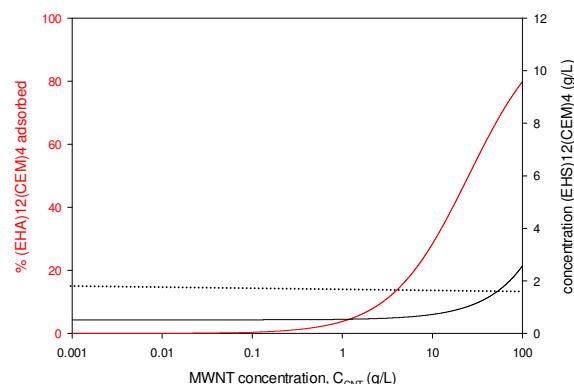
Based on the aforementioned results, we have prepared a series of polymeric surfactants which are either diblock copolymers, random copolymers or star copolymers (Figure 1). For that purpose, the Reversible Addition Fragmentation chain Transfer (RAFT) polymerization process was used. The copolymer contained two building blocks, one which was solvophilic (for example acrylic acid in water, or EHA in isoctane and THF) and the other one which was nanotubephilic (such as butyl acrylate in water and CEM monomer in organic solvent). For each set of dispersion experiments, Langmuir absorption isotherms have been established by varying temperature and the nature of electrolytes. Interestingly, for the same composition ( $n$  and  $m$  in Figure 1), the statistical copolymers (random arrangement of the units along the chain) are the best dispersant, whereas the diblock copolymers are the worst. Dispersion have also been studied by Raman spectroscopy (RBM bands), AFM, TEM microscopy (Figure 2) and broadband dielectric spectroscopy. Raman spectra indicate that there is no significant modification of the tubes before or after dispersion (or even once encapsulated, see below) : the intensity of the D band which is characteristic of sp<sup>3</sup> defaults ( $1342\text{ cm}^{-1}$ ) remains unchanged relative to the intensity of the G1 and G2 band ( $1565$  and  $1589\text{ cm}^{-1}$ ).



**Figure 2.** TEM photos of A) MWNT before dispersion, B) after dispersion C) after dispersion and polymerization (dispersant polymer  $(AA)_4(BA)_{10}$  – solvent : water)

With the values of  $\Gamma_s$  and  $a$  in hand, it is also possible to predict the surfactant concentration necessary to cover 90% of the surface at a given CNT concentration (Fig 3) – a coverage which we believe should be sufficient to ensure colloidal stability under most conditions. One striking feature of a Langmuir isotherm is that the concentration of

surfactant free in solution,  $C_{free}$ , only depends on  $\Gamma/\Gamma_s$ , and not on the CNT concentration (as clearly shown in Equation 2). Thus, in order  $\Gamma/\Gamma_s = 0.9$ ,  $C_{free} = 0.9/0.1 a = 9 a$ , and the total concentration of surfactant which is by definition greater than  $C_{free}$  must be greater than  $9 a$  (horizontal dashed line in Fig 3). Such calculations have been performed with the values of  $\Gamma_s$  and  $a$  of  $(EHA)_{12}(CEM)_4$  in isoctane. In comparison to the curves we have presented in the past for dispersion of MWCT by SDS [3] in water, it is clear that much more surfactant is needed to disperse MWNT organic medium, that is to say most of the surfactant is free in the solvent. For example, when the surface of a 1g/L MWNT suspension is covered at 90% (Fig. 7c),  $C_{free} = 1.8\text{ g/L}$ , but only 6% of the dispersant is adsorbed at the surface.



**Figure 3.** % dispersant adsorbed at the surface of the MWCNT vs concentration of CNT when the surface of is saturated at 90% (using the values of  $a$  and  $\Gamma_s$  of  $(EHA)_{12}(CEM)_4$ )

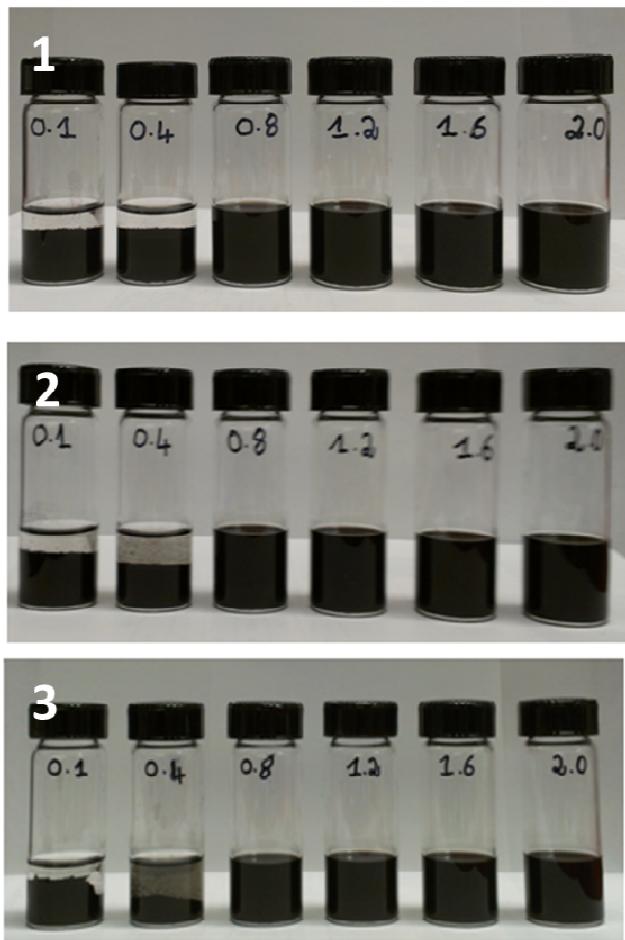


Figure 4 Dispersion of MWNT (1 g/L) by  $(EHA)_{12}(CEM)_4$  in isoctane. 1. The dispersion has been sonicated and left to settle for 1 day. The initial concentration of  $(EHA)_{12}(CEM)_4$  (in g/L) is indicated on each vial. 2. The dispersion has been centrifuged, the MWNT separated and washed with isoctane, then redispersed in isoctane by sonication. 3. The separation-washing procedure has been repeated.

Since the dispersion process is an intrinsically wasteful process (i.e. most of the dispersant is free in the solvent), we have endeavored to separate the CNTs from the solvent, to wash them with the solvent and to redisperse them (by sonication). In the case of the low molecular weight dispersant, the redispersion cannot occur : all the surfactant (either free or adsorbed) has been removed during the washing procedure indicating a rapid equilibrium between both states. By contrast, for polymeric surfactants the redispersion occurs smoothly (Figure 4). Analysis of the solution indicates that after washing, no surfactant is free in solution, however the surface coverage of the MWNT remains unchanged. Therefore, the adsorption of the dispersant is irreversible – and the dispersed CNTs can be separated from the surfactant free in solution.

Once the CNTs are well dispersed, it is then possible to continue the RAFT polymerization process (Figure 2C) [5]. As the RAFT polymerization is a so-called living process the polymerization results in the formation of an asymmetric block copolymer composed of a short surface active block (the dispersant) and a long hydrophobic block (as the quantity of monomer is larger than the dispersant). Since the dispersant is adsorbed at the surface of the CNT, the hydrophobic block effectively forms a continuous shell of polymer around the CNT. In short, the CNT is trapped in a shell of hydrophobic polymer covalently anchored to the dispersant. Importantly, although the use of a RAFT polymerization process is required to allow chain-extension of the dispersant by styrene (or MMA), it is not our intent to prepare polymers with a narrow molecular weight distribution: for an experiment performed in the absence of CNT, the block copolymer prepared under similar conditions has a polydispersity index of 1.5.

The encapsulation process was found to be efficient both in water and in organic solvent, as long as the polymer used to form the sheath is not soluble in the solvent. However, attempts to form sheaths of thickness larger than 5 nm failed. Nonetheless, we found that the presence of a sheath allowed the compatibilization of the CNT inside a polymeric matrix, resulting in the formation of nanocomposites devoid of aggregates.

This study has allowed us to elaborate a strategy for successful dispersion of nanotubes followed by their encapsulation in a variety of polymers. We are currently investigating the properties of the resulting dispersions either to form transparent electrodes once dried, or to form nanocomposites once formulated with a polymeric resin.

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