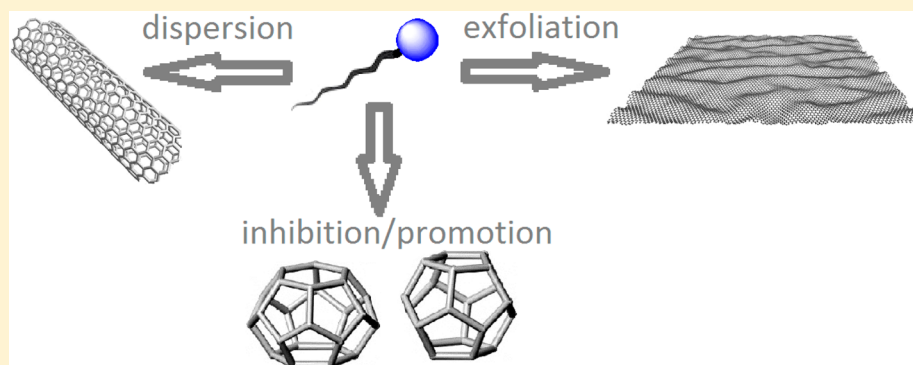


## Optimizing the Interactions of Surfactants with Graphitic Surfaces and Clathrate Hydrates

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**ABSTRACT:** Surfactants are amphiphilic molecules active at the surface/interface and able to self-assemble. Because of these properties, surfactants have been extensively used as detergents, emulsifiers, foaming agents, and wetting agents. New perspectives have been opened by the exploitation of surfactants for their capacity to interact as well with simple molecules or surfaces. This feature article gives an overview of significant contributions in the panorama of the current research on surfactants, partly accomplished as well by our research group. We look at several recent applications (e.g., adsorption to graphitic surfaces and interactions with hydrate crystals) with the eye of physical organic chemists. We demonstrate that, from the detailed investigation of the forces involved in the interactions with hydrophobic surfaces, it is possible to optimize the design of the surfactant that is able to form a stable and unbundled carbon nanotube dispersion as well as the best exfoliating agent for graphitic surfaces. By studying the effect of different surfactants on the capacity to favor or disfavor the formation of a gas hydrate, it is possible to highlight the main features that a surfactant should possess in order to be devoted to that specific application.

### 1. INTRODUCTION

Surfactants are amphiphilic molecules composed of a hydrophilic polar headgroup and a nonpolar or hydrophobic part that is compatible with organic solvents. This dual nature endows surfactants with unique solubilizing and interfacial features that drive their physicochemical behavior. One of the main characteristics of surfactants is their tendency, in dilute aqueous solutions, to self-assemble and form aggregates by exposing polar headgroups to water and segregating hydrophobic tails from water. Various molecular architectures result from this self-assembly. Depending upon the type of surfactant and the solution conditions, spherical or rodlike aggregates or bilayers may form.<sup>1</sup>

Israelachvili described the self-assembly as directed by a critical packing parameter (CPP) depending on the volume ( $v$ ), the surface area of the polar headgroup ( $a$ ), and the length ( $l$ ) of each surfactant molecule (i.e.,  $CPP = v/l \times a$ ).<sup>2</sup> A CPP below  $1/3$  favors the micellar arrangement,  $1/3 < CPP < 1/2$  favors cylindrical micelles, and  $1/2 < CPP < 1$  promotes two-dimensional bilayers and spherical bilayers containing an encapsulated aqueous phase called vesicles.

Despite the importance of this multiform behavior, we have been interested over the years mainly in exploiting the capacity of these amphiphilic molecules to interact not only with themselves but also with other molecules and surfaces.

The aim of this feature article is to illustrate some of the main achievements recently attained from the exploitation of amphiphilic molecules in the framework of surface and colloid science, materials science, and energy storage, providing an up-to-date overview focused on the research activity of the present authors, including future directions and perspectives in the field.

### 2. SURFACTANT ADSORPTION ONTO CARBON-BASED SURFACES

Pristine carbon nanotubes (CNTs)<sup>3</sup> possess unique mechanical, optical, and electronic properties<sup>4</sup> that are often lost in aggregated CNTs and difficult-to-process bundles. Analogously, the extraordinarily high mechanical stiffness and exceptional high thermal and electrical conductivity<sup>5</sup> that render graphene a very interesting material for a wide range of applications are maximized in nonagglomerated graphene sheets<sup>6</sup> and in single-layer nonfunctionalized graphene.<sup>7</sup> Simple solubilization of these materials in proper solvents is not viable because CNTs and graphene possess a very low solubility in both organic and aqueous solvents.

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Experimental data highlighted that the dispersion of CNTs at relatively high concentration can be obtained when the solvent and the nanotube surface energies match; nevertheless, water is not among these solvents.<sup>8</sup> Sonication favors their dispersion, although they quickly tend to reaggregate into packed ropes and entangled networks or multilayer graphene, respectively, as a result of the strong van der Waals interactions between carbon-based surfaces.<sup>9</sup>

The key point in preventing CNT–CNT or the graphene–graphene approach is to functionalize them in order to create a gap between graphitic surfaces and favor solubilization in aqueous solvents. Functionalization can be achieved by both covalent and noncovalent strategies. Many examples of effective covalent functionalization have been published, the most widely used being oxidation<sup>10,11</sup> and the Prato reaction.<sup>12,13</sup> The disadvantage of this method is that covalent functionalization may alter the valuable electronic properties of carbon nanotubes or graphene.

The use of surfactants has been widely investigated as an alternative strategy to reach an improved processability of these materials as a result of their capacity to adsorb onto carbon surfaces and thus noncovalently functionalize them. The advantage of this strategy is the preservation of the honeycomb lattice and thus the maintenance of the relevant extended  $\pi$ -electron networks of these materials. In particular, owing to the amphiphilic nature of surfactants, this noncovalent functionalization allows the dispersion of hydrophobic carbon-derived materials in aqueous solutions.

To favor the unbundling and water dispersion of carbon nanotubes, many commercial dispersing agents have been used in the past decade for the preparation of unbundled CNTs and few-layer graphene dispersions. Sodium dodecyl sulfate (SDS) and sodium dodecyl benzenesulfonate (NaDDBS) have been demonstrated to be particularly effective, dispersing in water as much as 45 and 65  $\mu\text{g mL}^{-1}$  CNT starting from a surfactant/CNT ratio of 10:1.<sup>14,15</sup> Well-exfoliated carbon nanotubes have also been obtained by using sodium cholate (SC) that nonetheless is less effective than the above-mentioned surfactants, dispersing 25  $\mu\text{g mL}^{-1}$  at a surfactant/CNT ratio of 100:1.<sup>14</sup> Among CNT aqueous dispersing agents, ammonium surfactants have shown less promise with respect to the widely investigated anionic surfactants; nevertheless, the ones most commonly cited have been dodecyl trimethylammonium bromide (DTAB) and cetyltrimethylammonium bromide (CTAB).<sup>14,16</sup>

Similarly, 2.6 mM aqueous SDS was able to disperse as much as 0.2  $\text{mg mL}^{-1}$  graphene after 1 h of sonication followed by centrifugation at 500 rpm for 15 min, but the exfoliation was limited to multilayer graphene (i.e., thickness from 8 to 60 nm). Nevertheless, the concurrent addition of ethanol enabled the dispersion of 2.1  $\text{mg mL}^{-1}$  single or few-layer graphene 0.8–2 nm thick.<sup>17</sup> On the other hand, 0.23 mM aqueous SC was able to disperse 0.3  $\text{mg mL}^{-1}$  graphene by using up to 430 h of tip ultrasonication.<sup>18</sup>

These surfactants act by exposing their hydrophobic portions to the carbon surfaces in order to promote van der Waals,  $\pi$ – $\pi$ , CH– $\pi$ , and hydrophobic effects while orienting their hydrophilic portions toward the aqueous phase.

Despite the dispersing ability of surfactants being the subject of a relevant number of papers, a lot has to be further studied and the design of the optimum aqueous dispersant for these carbon-based surfaces therefore appears to be very appealing.

**2.1. Effect of  $\pi$ – $\pi$  Interactions.** The role of  $\pi$ – $\pi$  interactions in the dispersion and debundling of single-walled carbon nanotubes (SWCNTs) is well known. Different authors

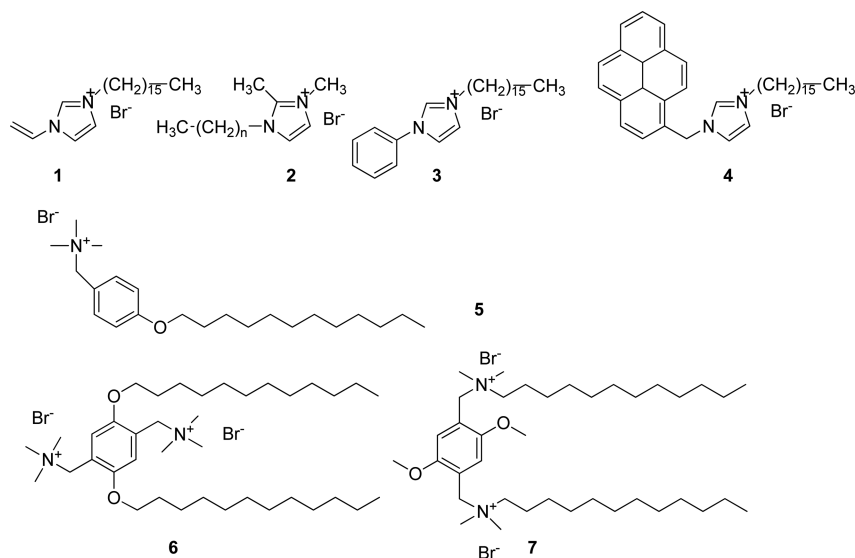
have reported systematic studies on the capacity of polycyclic aromatic hydrocarbons (PAH) to interact both with CNTs and graphene sheets. PAH molecules of lower mass were demonstrated to be more effective than higher-mass PAH in dispersing SWCNTs bundles.<sup>19</sup> In particular, the more planar and rigid polyacenes were able to better debundle SWCNTs with respect to the polyphenyl counterparts in which each phenyl unit is free to rotate relative to the other.<sup>19</sup> Similarly, graphene sheets were noncovalently functionalized and dispersed in water by using pyrenebutyric acid thanks to strong  $\pi$ – $\pi$  interactions between the pyrene moiety and graphene surface.<sup>20</sup> Björg et al.<sup>21</sup> found that the adsorption of neutral polyaromatic molecules on graphene was driven by  $\pi$ – $\pi$  interactions in terms of a complex combination of dispersive and electrostatic interactions, with the former interactions docking the aromatic molecule on graphene and short-range electrostatic interactions stabilizing the complex.

Comparably,  $\pi$ – $\pi$  interactions have been demonstrated to be essential in explaining the extraordinary capacity of ionic liquids (ILs) to favor carbon nanotube debundling<sup>12,22</sup> and graphene exfoliation<sup>23</sup> when ground together or sonicated with them. Following this discovery, the ability of ionic-liquid-based surfactant 1-hexadecyl-3-vinylimidazolium bromide (**1**) (Figure 1) to disperse single-walled carbon nanotubes (SWCNTs) in water has been investigated. The sonication of SWCNTs with aqueous solutions of **1** at comparable surfactant/SWCNT ratios ensured a dissolution activity of **1** that was twice as much as that of SDS, 20% higher than that of cetyltrimethylammonium bromide (CTAB), and similar to that of NaDDBS.<sup>24</sup> This is indicative of the fact that both van der Waals and  $\pi$ – $\pi$  interactions come into play. The former interactions are due to molecular interactions among surfactant alkyl chains forming an assembled layer on the graphitic surface<sup>25,26</sup> as well as surfactant alkyl chains and carbon surfaces<sup>27</sup> (section 2.2). The latter interactions are brought about by the vinylic moiety with graphitic surfaces. The role of the aromatic imidazolium ring in this case is twofold because it can either interact via cationic  $\pi$ – $\pi$  interactions with the graphitic surface or act as a polar head and expose itself to the bulk water.<sup>28,29</sup> In agreement with this hypothesis is the evidence, obtained through fully atomistic molecular dynamics (MD) simulations, that the adsorption of a small number of cationic surfactant molecules to carbon-based surfaces occurs via favorable head-on binding<sup>30</sup> rather than through the expected tail-on binding.

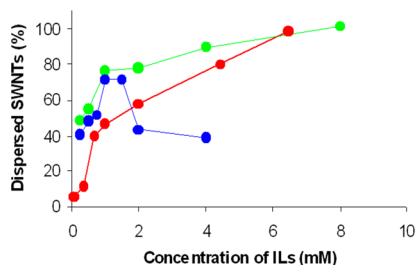
It is noteworthy that the investigated ionic-liquid-based surfactant **1** was twice as effective at solubilizing CNTs as 1,2-dimethyl-3-alkylimidazolium bromides (**2**).<sup>15</sup> It is likely that the presence of a methyl in the 2 position and the overall lack of an additional double bond disfavor the affinity of **2** for both the nanotubes and bulk water.

By synthesizing structural analogues of **1**, it was possible to clarify the role of phenyl or polyaromatic rings in controlling the affinity for the carbon nanotubes. Despite the substitution of the vinyl group in the 3 position of the imidazolium ring with a phenyl (**3**) or a pyren-1-ylmethyl moiety (**4**) rendering these surfactants more hydrophobic than **1**, their ability to disperse SWCNTs was related to their respective hydrophobic surface and concentration.<sup>28</sup> The SWCNTs' dispersing ability of **1** was relatively low at low surfactant concentrations but increased linearly on increasing the concentration of **1** as a result of the progressive adsorption of **1** onto the nanotube surface (Figure 2).

A relatively high dispersing activity followed by a leveling-off effect was observed instead for **3**. This trend was related to its larger hydrophobic surface area as compared to that of **1**<sup>28</sup> and



**Figure 1.** Investigated ionic-liquid-derived and ammonium-rich surfactants.



**Figure 2.** Percentage of SWCNTs dispersed with the investigated ILs: 1 (red spots), 3 (green spots), and 4 (blue spots). Reprinted with permission from ref 28. Copyright 2011, Royal Society of Chemistry.

the subsequent saturation of the nanotube surface at 1.0 mM **3** (i.e., the lowest surfactant concentration ensuring the maximum SWCNT dispersion). However, the decreased dispersion ability monitored for **4** above 1.0 mM was ascribed to its much lower aqueous solubility with respect to the other surfactants or its preference to form micelles rather than adsorb onto the nanotube surface at concentration of surfactants well above its CMC.

Following Strano et al.'s evidence,<sup>31</sup> the dependence of the CNTs' dispersing activity of **1** and **3** on surfactant concentration can instead depend on a trade-off between their surfactant affinity for the CNTs and the increase in ionic strength of the bulk solution on increasing the surfactant concentration. Very interestingly, they discovered that the adsorption of the planar anionic surfactant sodium cholate (SC) to graphitic surfaces is connected to the radius of carbon nanotubes and the surfactant concentration. According to their large-scale coarse-grained molecular dynamics simulations at low SC concentrations (<10 mM), small-radius SWCNTs were characterized by a lower surface coverage with respect to SWCNTs with a larger radius. The large local curvature of the former SWCNTs can in fact reduce the interactions of the planar molecule with the graphitic surface. However, at high SC concentrations (>20 mM), small-radius SWCNTs show a higher SC adsorption as a result of the reduced electrostatic repulsions between the negatively charged cholate headgroups of the adsorbed SC molecules as a consequence of the increased ionic strength. If this were the case, then the increased percentage of dispersed SWCNTs observed on increasing the concentration of **1** and **3** is due to their tendency

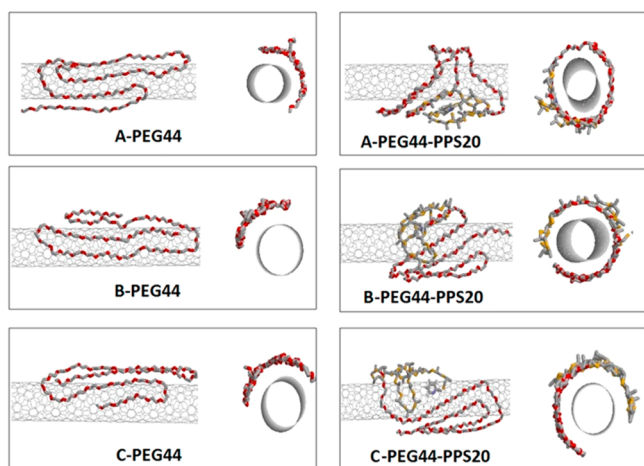
to prevalently adsorb to SWCNTs of small radius (as evidenced also by NIR phospholuminescence data)<sup>28</sup> and to the fact that on increasing the ionic strength with surfactant concentration, the density of adsorbed surfactants on graphitic surfaces increases.<sup>31</sup>

## 2.2. Hydrophobicity and van der Waals Interactions.

van der Waals interactions and the length of the surfactant alkyl chain are recognized to be essential to controlling the affinity of the surfactant for the surface of graphene-based materials and enhancing both the dispersion effectiveness and efficiency.

The chain length effect can be analyzed when considering SWCNT dispersions produced by homologous series of surfactants such as alkyltrimethylammonium bromides. Fernandes et al.<sup>32</sup> highlighted a linear decrease in the surfactant concentration required to achieve the maximum CNT dispersion as well as a reduction of the number of surfactant molecules per unit area on increasing the number of carbon atoms in the alkyl chain. Because CMC decays exponentially with the number of carbons in the alkyl chain,<sup>33</sup> the observed linear correlation shows that van der Waals interactions other than lateral attractive interactions between adjacent adsorbed molecules (i.e., widely recognized as responsible for self-aggregation) come into play in SWCNT dispersions. Following this evidence, the enhanced hydrophobic character of a surfactant with increasing alkyl chain length is demonstrated to favor its tendency to adsorb onto hydrophobic carbon-based surfaces.

We investigated the ability of the hydrophobic portion of a surfactant to adsorb onto the nanotube surface by using atomistic MD simulations based on a well-assessed computational technique termed essential dynamics (ED). We studied the system SWCNT/PEG44-PPS20 (where PEG44-PPS20 is the diblock poly(ethylene glycol-*bl*-propylene) sulfide copolymer formed by the hydrophilic PEG44 and hydrophobic PPS20 portions) in the presence of water molecules in solution and compared its behavior to that of SWCNT/homopolymer (PEG44).<sup>34</sup> The data obtained highlight that the hydrophobic nature of the PPS20 block systematically ensures a higher SWCNT surface coverage (Figure 3), a higher water depletion from the nanotube surface, and thus a much lower degree of water ordering when compared to that of the PEG44 homopolymer. Besides, despite the substitution of oxygen atoms with sulfur atoms being expected to impart a higher hydrophobicity to the PPS hydrophobic domain as compared to the

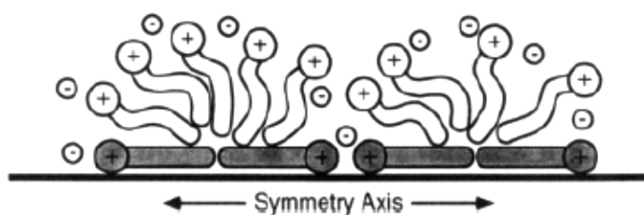


**Figure 3.** Representative structures of homopolymer PEG with 44 monomer units (PEG44) and PEG–PPS containing 44 and 20 monomer units of PEG and PPS, respectively (PEG44-PPS20), adsorbed on SWCNT as obtained by essential dynamics. Reprinted with permission from ref 34. Copyright 2012, American Chemical Society.

oxygen analogue, no evidence arose from our study of the positive effect of PPS20 in enhancing the affinity for SWCNTs. On the other hand, the spread of the polymer on the nanotube surface (Figure 3) was particularly high for the hydrophilic PEG44 chains as well, with a parallel arrangement of strands with respect to the direction of the tube axis.

Many studies have investigated the assembly of surfactants onto hydrophobic surfaces by reporting that there are two major factors that control this assembly: (a) the affinity of the alkyl chains for the surface, which is driven by hydrophobic interactions associated with the entropically controlled water molecule desolvation from the graphitic surface,<sup>28</sup> and (b) the prevailing orientation of the alkyl tail on the surface, which span from a completely flat to a perfectly perpendicular arrangement to the basal plane of graphite. Because experimental evidence on the configurational arrangement of adsorbed surfactant on hydrophobic surfaces is relatively complex to realize, only few direct data are available. Diverse hypotheses, based on MD calculations as well as on surfactant organization onto graphitic surfaces, have been formulated. They span from a random surfactant monolayer<sup>27,34</sup> for poorly hydrophobic surfactants to well-defined surfactant self-aggregates<sup>26</sup> for more hydrophobic molecules.

Atomic force microscopy experiments revealed that surfactants would preferentially form hemimicelles<sup>35</sup> or hemicylinders<sup>36</sup> (Figure 4) when adsorbed onto carbon nanotubes



**Figure 4.** Perpendicular cross section through two neighboring hemimicelles along a graphitic surface. Reprinted with permission from ref 36. Copyright 1994, American Chemical Society.

or graphitic surfaces, respectively, with the only exception of the first surfactant layer that showed a periodicity of twice the

molecular length, consistent with head-to-head and tail-to-tail self-assembly.<sup>29,36</sup>

Similarly, cryogenic transmission electron microscopy analyses (cryo-TEM) imaged the presence of discrete micelle aggregates adsorbed onto SWCNT side walls.<sup>37</sup>

Very recently, small-angle neutron scattering techniques demonstrated that SWCNTs are instead solubilized in cylindrical micelles formed by a central core of small nanotube bundles surrounded by an adsorbed layer of extended SDS molecules.<sup>25</sup> If this were the case, then the increased effectiveness of the adsorption with alkyl chain length arises from cooperative surfactant alkyl chain interactions rather than surfactant alkyl chain–surface interactions.

From these few examples, it can be gathered that both surfactant alkyl chain–surfactant alkyl chain and surfactant alkyl chain–carbon-based surface van der Waals and hydrophobic interactions are strategic in directing the exfoliation and debundling ability of the surfactants toward graphene and CNTs.

**2.3. Roles of Hydrophilicity and Polarity.** The role of the solubility of the surfactant in water and therefore the features of the surfactant polar headgroups are equally important. Despite the presence of a highly hydrophobic group that increases the affinity of the surfactant toward nanotube might favor intermolecular interactions among adsorbed molecules, both for enthalpic as well as entropic effects as stated above, a too strongly hydrophobic domain might suppress the solubility of the molecule in water, thus preventing its ability to disperse the nanotube in an aqueous environment.<sup>28</sup> Therefore, an effective dispersing agent of carbon nanotubes should have a well-defined balance between the solvophilic and the solvophobic domains of the molecule.

MD simulations can provide<sup>28</sup> a semiquantitative indication of the affinity of each dispersing agent toward SWCNTs. MD on 1, 3, and 4 (Figure 1) evidenced that the presence of a moiety that is too solvophobic on the imidazolium ring disfavors its displacement from the nanotube surface. The reduced tendency of the imidazolium ring to behave as a polar head decreases its interactions with bulk water molecules and lowers the ability of the corresponding surfactant to disperse CNTs.

This evidence is in agreement with  $\zeta$ -potentials measurements recorded for SWCNT dispersions prepared with alkyltrimethylammonium bromides of different alkyl chain lengths. Despite stable dispersions being characterized by  $|\zeta| > 30$  mV, the observed increase in  $\zeta$  potentials of surfactant-coated SWCNTs on increasing chain length is again indicative of the need for the surfactant to have a precise balance between the hydrophilic and hydrophobic domains to act as a good dispersant.<sup>32</sup>

Although simulations may depend on the reliability of the force field implemented, Striolo et al.<sup>38</sup> calculated that the stabilization of carbon nanotubes in water depends on how strongly dispersing agents adsorb on the nanotube surface as well as whether they present hydrophilic groups that are able to extend toward the aqueous phase. As reported above, the developed simulation-assisted Derjaguin–Landau–Verwey–Overbeek (DLVO) theory allowed Strano et al.<sup>31</sup> to quantify the potential energy barrier height required to impart colloidal stability to SWCNTs or graphene dispersions and to find that the best dispersant adsorption is associated with high ionic strength in the bulk phase.

Similarly, Coleman et al.<sup>39</sup> demonstrated that the concentration of graphene sheets obtained by tip sonication for 30 min at 560 W in a 100 mL aqueous surfactant solution with 500 mg of graphite powder depends strongly of the  $\zeta$  potential of the

surfactant-coated graphene sheets. In particular, SC was able to disperse as much as  $26 \mu\text{g mL}^{-1}$  graphene, whereas only  $11 \mu\text{g mL}^{-1}$  graphene dispersions were obtained with SDS under the same experimental conditions. A linear dependence of graphene concentration on the repulsive electrostatic potential barrier was observed, indicating that repulsive electrostatic interactions stabilize the surfactant-coated graphitic sheets against aggregation.

As far as nonionic surfactants are concerned, it is classically recognized that the amount of dispersed graphene scales linearly<sup>33</sup> with the steric repulsion barrier of the used nonionic surfactant. This dependence is related to the osmotic repulsion generated by the hydrophilic groups of the adsorbed dispersant, extending from the graphene surface toward the bulk solution. Examples of effective nonionic surfactants widely used for dispersions of graphitic materials are amphiphilic block copolymers.<sup>40,41</sup> Steric repulsion between hydrophilic poly(ethylene glycol) moieties of Pluronic P-123 allowed Guardia et al. to disperse as much as  $1 \text{ mg mL}^{-1}$  graphene via 2 h of ultrasonication, whereas  $1.5 \text{ mg mL}^{-1}$  graphene dispersions were obtained by simply increasing the sonication time to 5 h.<sup>42</sup>

Contrary to these results and as mentioned above (section 2.2), our MD simulations, performed on SWCNT/homopolymer (PEG44),<sup>34</sup> did not evidenced hydrophilic PEG44 chains extending and swelling in bulk water. It is likely that this latter behavior is associated with the fact that our simulations considered much lower surface densities than were experimentally relevant.

**2.4. Surfactant CMC and Dispersing Activity.** Indeed, conventional surfactants, such as cetyltrimethylammonium bromide (CTAB) and NaDDBS, disperse CNTs at surfactant/CNT weight ratios of around or higher than 10,<sup>14</sup> but they appear not to be able to effectively disperse SWCNTs below their CMC.

Keeping in mind the above-mentioned dependence of the dispersing ability on the capacity of the dispersant to saturate the CNT side walls, we synthesized *N*-[*p*-(*n*-dodecyloxybenzyl)]-*N,N,N*-trimethylammonium bromide (**5**) and two related gemini surfactants, 2,5-bis(*n*-dodecyloxy)-1,4-bis(*N,N,N*-trimethylammoniomethyl)phenyl bromide (**6**) and 2,5-dimethoxy-1,4-bis[*N*-(*n*-dodecyl)-*N,N*-dimethylammoniomethyl]phenyl bromide (**7**) (Figure 1).<sup>43</sup>

Gemini surfactants typically possess two hydrophobic tails and two polar headgroups linked by a spacer, which may be rigid or flexible. These surfactants have great potential due to the recognized lower CMC with respect to a conventional single-chain surfactant, a high hydrophobic microdomain, and a variety of micellar aggregate morphologies spanning from spherical to cylindrical micelles due to their relatively high CPP.<sup>44</sup>

All of the investigated salts have been demonstrated to disperse SWCNTs quite well, being able to disperse CNTs at exceptionally low surfactant/CNT weight ratios (e.g., 1.5, 1.7, and 2.4 for **5**, **6**, and **7**, respectively). Although single-chain surfactant **5** appears not to be able to effectively disperse SWCNTs below its CMC, gemini surfactants disperse double the number of nanotubes with respect to **5** and even at surfactant concentrations well below their CMC values, in agreement with previous measurements on analogous gemini surfactant (i.e., the hexyl- $\alpha,\omega$ -bis(dodecyldimethylammonium) bromide).<sup>45</sup>

The dispersing ability manifested by a single-tail surfactant above its CMC may therefore be ascribed to the fact that the aggregation of surfactant (i.e., tail-to-tail hydrophobic interactions between the surfactant alkyl chains with the formation of a patchy monolayer around the SWCNTs or surfactant micelles of different shape, see section 2.2) promotes the effect. The higher efficiency of the CNT dispersing agent of gemini surfactants compared to that of the single-tail surfactant might be

attributed to a higher surface coverage due to the presence of two alkyl chains for each surfactant and compact alignment on the nanotube surface (section 2.2) as well as to the higher charge capacity per single molecule of surfactant (section 2.3). Indeed, gemini surfactants exhibit favorable packing<sup>44</sup> as a result of the capacity of the spacer to force the pair of ionic groups to reside in a less-space-filling geometry relative to that of two conventional single-chain surfactants. In conclusion, the surfactant concentration at which the CNT dispersion occurs depends on the total surface area of CNT available and the capacity of the surfactant to adsorb onto CNT side walls.

A recent study<sup>32</sup> indicated that micelles are not essential for inducing SWCNT dispersions because the maximum CNT dispersion and the number of surfactant molecules per unit CNT area depend linearly on chain length, suggesting that micelles could rather act as reservoirs for surfactant molecules or perhaps favor the initial exfoliation process. Indeed, the CMC of the surfactant in the CNT dispersion was estimated to be 10–50% higher than the CMC of the neat surfactant depending on nanotube loading.<sup>46</sup>

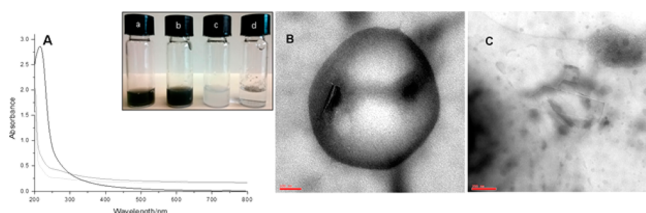
On the other hand, it is known that a decrease in CNT dispersibility was observed at high enough surfactant concentration (i.e., surfactant concentration >10CMC) due to depletion-driven flocculation,<sup>47</sup> as demonstrated also by semiquantitative measurements of SWCNT dispersions using small-angle neutron scattering.<sup>48</sup>

Despite the fact that CNT dispersions could be obtained at surfactant concentrations below the relevant CMC, the role of cooperative surfactant alkyl chain interactions cannot be neglected, and surfactant preaggregates and self-assembly are essential for ensuring proper adsorption (section 2.2).

**2.5. Debundling and Exfoliation of Carbon-Based Derivatives.** Despite surfactants aiding the debundling of carbon nanotube aggregates, a big difference exists between the exfoliation of carbon nanotubes and the exfoliation of graphite. The former exfoliation involves the aggregation of preformed carbon nanotubes. Because of strong van der Waals interactions among carbon nanotube side walls, they tend to aggregate in bundles and exfoliation is necessary in order to process them. However, the exfoliation of graphite represents a top-down strategy for the preparation of graphene sheets from the built-in graphite crystals. In this regard, surfactants are extremely useful not only for the achievement of good nonfunctionalized graphene dispersions but overall because they represent an elected and scalable method for the preparation of monolayer and few-layer graphene aqueous dispersions.<sup>49</sup>

Coleman et al.<sup>49</sup> realized a good exfoliation of graphite with  $10 \text{ mg mL}^{-1}$  NaDDBS in aqueous solution achieving  $50 \mu\text{g mL}^{-1}$  graphene dispersions composed of ca. 3% monolayer graphene and ca. 40% flakes with fewer than five layers of graphene. The so-obtained exfoliated graphene flakes were also demonstrated to be stabilized against reaggregation owing to the relatively large potential barrier originating from repulsion between surfactant-coated sheets.<sup>49</sup>

We exfoliated graphite and stably dispersed graphene by bath sonicating for 2 h graphite with 1-palmitoyl-2-oleoylphosphatidylcholine (POPC) large unilamellar vesicles prepared by the hydration of a lipid POPC film, obtained by evaporating<sup>50–52</sup> the chloroform solvent in a rotary evaporator (Figure 5).<sup>53</sup> Raman spectroscopy evidenced in the samples the presence of nonoxidized double-layer graphene as well as amphiphilic phospholipid molecules organized in bilayers, thus confirming the hypothesis of graphene nanosheets sandwiched into POPC bilayers with almost



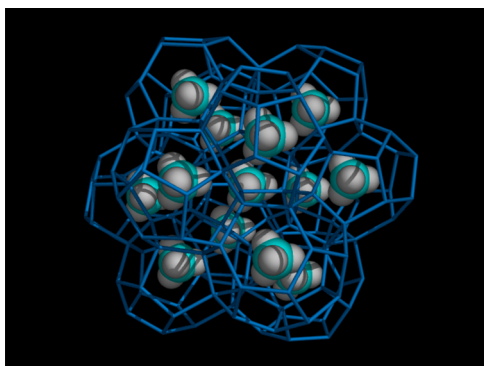
**Figure 5.** (A) UV-vis spectra of graphene-loaded liposomes in phosphate buffer (light-gray line) in Milli-Q water (dark-gray line) and empty liposomes (black line) used as a baseline. (Inset) Digital pictures of vials containing graphene-loaded liposomes in (sample a) Milli-Q water and (sample b) phosphate buffer, (sample c) empty liposomes in phosphate buffer, and (sample d) graphite in Milli-Q water after sonication for 2 h in the absence of phospholipids. (B) TEM images of GO-embedding liposomes magnified 85 000 $\times$  and (C) graphene sheets magnified 50 000 $\times$ . Scale bars are 100 nm in B and 200 nm in C. Adapted from ref 53, following Creative Commons Attribution 3.0 Unported License, 2015.

no effect on its thickness and liposome dimensions. Atomic force microscopy (AFM) measurements confirmed the exfoliation of graphite to few-layer graphene.

Similarly, hydrophobic aromatic hexa-*peri*-hexabenzocoronene (HBC) functionalized with hydrophilic carboxy groups was used to exfoliate graphite and disperse graphene in water.<sup>54</sup> As expected,  $\pi$ - $\pi$  interactions between the large aromatic core of HBC and graphene was shown to mediate the exfoliation of graphite into graphene whereas bulky hydrophilic carboxylic groups favored the stabilization of the obtained aqueous dispersions.

### 3. EFFECT OF SURFACTANTS ON THE FORMATION OF CLATHRATE HYDRATES

Clathrate hydrates (also called gas hydrates) are studied equally intensively both as a practical subject and at a fundamental level.<sup>55</sup> Hydrates are solid, icelike inclusion compounds formed by the polyhedra of hydrogen-bonded water molecules, which contain a variety of small molecules (guest molecules), mainly gases such as H<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub>, and H<sub>2</sub>S, and also small organic compounds (e.g., cyclopentane (CP), tetrahydrothiophene (THT), and tetrahydrofuran (THF)). The geometry of the crystal structures formed depends on the nature, size, and shape of the guest molecule. Commonly reported structures are structure I (sI), structure II (sII) and structure H (sH) (Figure 6).



**Figure 6.** Molecular model of a methane clathrate hydrate. Methane occupies both large and small cages of the sI structure. Water molecules are omitted, and only cage-forming bonds are shown in blue.

For example, CO<sub>2</sub> or CH<sub>4</sub> forms structure sI, and a binary hydrate of H<sub>2</sub> plus THF forms structure sH.

### 3.1. Inhibition of Clathrate Hydrate Formation.

Industrial research on (natural gas) hydrates is mainly focused on flow assurance for the oil and gas industry, where huge amounts of methanol or glycols are used as thermodynamic inhibitors (i.e., acting to increase the pressure and/or decreasing the temperature of hydrate formation) to prevent the buildup of hydrate formation within oil and gas pipelines in cold regions and/or subsea lines.<sup>56</sup> In this field, novel approaches are being developed to replace the heavily polluting and expensive alcohol; indeed, the amounts of methanol or glycol needed may reach values of up to 50 wt % or higher, thereby raising economic and environmental issues. Attempts to solve the problem of pipeline hydrate formation have focused on the use of particular molecules that exert their inhibiting effect at much lower concentrations as compared to thermodynamic inhibitors. These compounds are known as low-dosage hydrate inhibitors (LDHIs), which are generally polymers or lower-molecular-weight molecules (notably surfactants) that act as either kinetic inhibitors (i.e., they increase the hydrate induction time) or antiagglomerants (AAs), which prevent the further agglomeration of formed hydrate particles. The LDHIs mainly affect the surface properties and are usually employed at concentrations of less than 4 wt %.

In general, the supramolecular mechanisms underlying the inhibition effects of LDHIs are poorly understood, partly because of the differences in molecular structures among the various LDHIs tested so far (e.g., vinylpyrrolidone-based polymers, polyacrylamides, poliactamides, alkylglucosides, onium salts, etc.). Moreover, many references relating to novel hydrate inhibitors are found in the patent literature, where the rationale at the basis of the observed effects may be of secondary concern and is not investigated in depth. In the last years, however, researchers have increasingly been interested in those supramolecular mechanisms as a way to gain insights into the basic processes of hydrate formation. York and Firoozabadi, for example, focus on the relationship between the structure and function of antiagglomerant surfactants.<sup>57</sup> Such an antiagglomerant acts by preventing the agglomeration of hydrate crystals, thus allowing their flowability (e.g., a pipeline without any blockage). For a surfactant to be effective as an AA, a number of structural features should be satisfied. The headgroup should have the ability to hydrogen bond with water, such as by carbonyl or amine groups, in order to compete with the formation of hydrogen-bonded hydrate cages. Surfactant headgroups should also be able to interact electrostatically (e.g., by quaternary ammonium moieties). AA surfactants can also have clathrate-forming headgroups, which may lead to a partial incorporation of the AA headgroup into a hydrate lattice. However, this feature may lead to the requirement of a higher concentration of the inhibitor as it tends to be taken into the crystal, thus also acting partially as a cofomer and possibly modifying the  $P$ - $T$  range of hydrate formation. It is also reported that a fundamental role in the activity of AAs has to be ascribed to the hydrophobic tail, which should render the forming hydrate crystallite more lipophilic and therefore dispersible in the hydrocarbon phase.<sup>58</sup> However, this explanation of the role of the hydrocarbon tail of surfactants is at odds with the well-known hydrate promotion effect of other families of surfactants, such as alkyl sulfonates and sulfates, which are being studied and developed to enhance hydrate formation in the field of natural gas storage and transportation,<sup>59</sup> as further detailed below (section 3.2). Another issue to be considered when using surface-active AAs is that water-in-oil emulsions may form under high oil cut conditions (i.e., related

to the prevalence of oil phases in the process stream). In that case, hydrate growth is limited to the size of the microemulsion, but if the emulsion is particularly stable, then phase separation at the end of the transportation process may become difficult and further treatments will be needed to obtain a product that meets the relevant quality standards.<sup>60</sup>

All of these issues point again to a strong necessity of developing a fundamental understanding of the structure–property relationships that govern the inhibition or promotion of hydrate formation by surfactant molecules. In this regard, the authors have developed a basic chemometric tool aimed at the prediction of the inhibiting properties of novel LDHIs.<sup>61</sup> The molecules studied in that work are both known inhibitors, in particular, tetra-alkylammonium surfactants and novel compounds that were not previously described. As relates to the latter, the study was focused on structural features, such as the introduction of moieties that could partially fit into the hydrate cage (e.g., a cycloalkyl or heterocyclic moiety) to induce the formation of partially closed hydrate cages and increase the strength of interaction between surfactant molecules and the hydrate crystals. As a general classification, the compounds studied can be defined as cationic, single-chain surfactants, and their short-chain analogs, as halide or mesylate counterions, twin-chain cationic surfactants, and sulfobetaines. Experiments were conducted in a custom apparatus<sup>62</sup> under constant-pressure conditions, as described elsewhere.<sup>61</sup>

Experimental data and molecular structures were then fed into a quantitative structure–property relationships (QSPRs) analysis, as implemented into the software package Volsurf+<sup>63</sup> to produce numerical descriptors for the 52 molecules in our data set. This software provides and analyzes these molecular descriptors and the relationship between the property/activity and the molecular structure. Basically, according to that approach, structural features are given numerical descriptors that are then correlated with the hydrate inhibition properties. However, the chemical “decoration” of a molecule generally affects more than one property because properties and structural features are related by complex multiparametric relationships, which requires a multivariate strategy. In the Volsurf+ approach, we have first collected property data sets, obtained by using specific experimental designs in order to minimize the number of experiments and produce homogeneous data. Then, through molecular modeling, molecular descriptors were obtained in terms of interaction energies, the structure of chemical moieties, and so forth. Nonsignificant or correlated (and hence redundant) descriptors were then eliminated, and those that showed correlations with the relevant properties were retained, thus obtaining a mathematical relationship between the experimental properties and structural descriptors of the molecule. This provided a prediction tool for designing novel molecules with tailored inhibition properties. According to this study, a good inhibitor should be approximately balanced in the hydrophilicity/hydrophobicity ratio per surface unit and have a wide polar surface and high water solubility.<sup>63</sup> Further characteristics that enhance the inhibition properties of a surfactant were shown to be a low partition coefficient between water/*n*-octanol and water/cyclohexane and a low critical packing value (which is correlated to the CMC). This analysis, with the appropriate changes, can also be applied to the design of hydrate promoters, which will be discussed below (section 3.2). This *in silico* method might also reduce the experimental time and reagent costs in the quest for novel LDHIs, allowing us to carry forward only compounds whose properties seem most promising. Following the information obtained with this QSPR approach, we have synthesized several novel cationic surfactants with variable

headgroup structure, chain number, and length. These molecules have been tested under static conditions (i.e., in the absence of hydrocarbon flow); most of them have been shown to variously inhibit methane hydrate formation. Before any estimation of industrial applicability, however, tests will be conducted in a flow loop facility before testing in the field.

**3.2. Promotion of Clathrate Hydrate Formation.** As mentioned above, surfactants may also promote hydrate formation; we might call them amphifunctional amphiphiles. It should be emphasized at this point that with the promotion of hydrate formation by a compound we refer to a kinetic promotion (i.e., either (i) a shortening of the induction time, which is the time needed for the first crystallites to form after the system has entered the hydrate stability region; (ii) an increase in the formation rate; and/or (iii) an increase of the occupancy, which is the proportion of water cages effectively filled by gas molecules with respect to the theoretical stoichiometry). A kinetic promotion, therefore, does not affect the thermodynamic parameters (pressure and temperature) under which a particular hydrate forms.

The fact of a surfactant being a promoter or an inhibitor depends on several factors, some of which are known. The charge of the headgroup is one major determinant of the resulting effect on hydrate formation; in fact, sulfate- and sulfonate-headed surfactants (e.g., SDS, alkyl benzenesulfonates, etc.) are among the best promoters known so far. The interest in hydrate promoter compounds arises when it was envisaged that a feasible alternative to liquefied natural gas storage and transportation could be developed on the basis of gas hydrates. In fact, natural gas hydrates can store up to 15 wt % gas (basically methane), which amounts to ca. 200 N m<sup>3</sup> gas per cubic meter of solid hydrate. This figure means, according to some calculations, that an industrial production chain for gas storage and transportation, which is based on hydrates, could lead to a cost reduction of ca. 24% in the small- to large-scale markets.<sup>64</sup> Another important aspect of gas hydrate technology will be its inherent safety because methane-charged hydrates are not vulnerable to explosion and do not require heavy-duty containers for their storage. A storage and transportation system based on hydrates is being actively developed by Mitsui Engineering and Shipbuilding in Japan. As far as gas storage and transportation are concerned, it was found that selected surfactants could improve the formation of hydrates, even in the absence of stirring. SDS (242 ppm), in particular, would speed up the formation of a highly charged hydrate by decreasing its induction time by ca. 700 times.<sup>65</sup> The mechanism by which SDS promotes hydrate formation was explained by Rogers<sup>65</sup> as a consequence of the formation of micellar aggregates that would increase the solubilization of methane into the micellar core, thus enhancing its concentration in water and promoting the process of hydrate formation. However, it turned out that things were less straightforward when it was speculated that the concentration of SDS employed to promote hydrates was much lower than its reported CMC. We therefore determined the CMC of several surfactants in water by measuring their conductivity vs concentration profiles under hydrate-forming conditions (2 °C, 40 bar methane) and under the same conditions with nitrogen. We also investigated sodium laurate (SL), sodium oleate (SO), 4-dodecylbenzenesulfonic acid (DBSA), and cationic dodecylamine hydrochloride (DAHC) and dodecyltrimethylammonium chloride (DTAC).<sup>59</sup> For SO, DBSA, and DTAC, CMC values were found to vary slightly under hydrate-forming conditions with respect to normal *P–T* conditions, whereas SDS, SL, and DAHC solutions underwent precipitation before reaching the CMC under hydrate-forming conditions.<sup>59</sup>

This led to the conclusion that micelles do not form for any surfactants in the concentration range where strong hydrate promotion was reported by Rogers.<sup>65</sup> We proposed that a kind of preorganization of water networks could be enacted by the surfactant molecules in solution, according to a hydrophobic hydration mechanism. However, this question is still being strongly debated.

**3.3. Storage of Hydrogen.** Surfactants have also been investigated in relation to the storage of hydrogen in clathrate hydrates. Until a few years ago, it was thought that hydrogen could not form hydrates because of its small size. In 2002, however, the first hydrogen hydrates were prepared under extreme pressure and/or temperature conditions (e.g., 200 MPa @ 294 K). This unleashed frantic research on the subject, paralleling the enthusiastic “gold rush” in the fuel cell industry of those years. The aim was, of course, that of improving the  $P$ – $T$  conditions of hydrate formation in developing a milder and safer technology for storing hydrogen to feed a fuel cell. THF was found to lower the formation pressure remarkably from 200 to 7 MPa at 7 °C by its action of filling the large cages and stabilizing the overall sII structure. The smaller cages were then able to accommodate hydrogen molecules.<sup>66</sup> However, from a practical standpoint, it was apparently impossible to form hydrates containing more than a fraction of 1% by weight. Strobel and Sloan et al.<sup>67</sup> recognized the need to decrease the size of ice particles to increase the surface-to-volume ratio in order to maximize hydrogen uptake. Another method for hydrogen storage is described in a patent by Peters and Sloan,<sup>68</sup> wherein the clathrate is formed starting from a composition of water and a coformer, the latter playing the role of reducing the pressure and/or increasing the temperature needed to form a clathrate hydrate of hydrogen. In the above attempts, the major problem was the lack of efficient mass transfer between the gaseous and the liquid and/or hydrate phases.

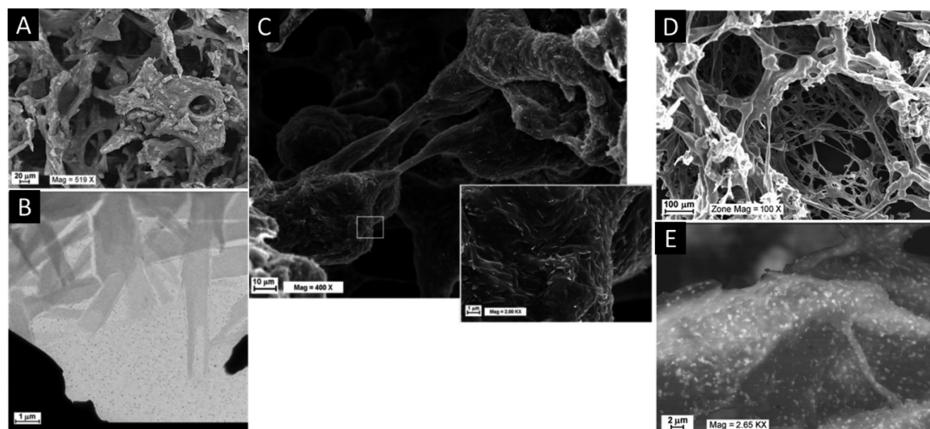
To form hydrate nanoparticles with a bottom-up approach, a process was devised starting with water-in-oil nanoemulsions (i.e., water pools or droplets a few nanometers across (3 orders of magnitude smaller than the smallest crushed ice particles of Sloan and co-workers)) that are stabilized by a monolayer of surfactant molecules (e.g., sodium dioctyl sulfosuccinate, docusate sodium) in a bulk organic solvent such as iso-octane or cyclopentane.<sup>69</sup> The system thus obtained (i.e., a nanoemulsion) was macroscopically homogeneous, and the water droplets could then be induced to form hydrate nanoparticles when the system was

placed under the appropriate  $P$  and  $T$  conditions. The extremely small sizes of those nanodroplets allowed for enhanced gas flux to be captured, with a resulting hydrogen hydrate formed within tens of minutes at nominal 1 wt %  $H_2$ . This nanoemulsion method is also advantageous in that the presence of an organic solvent allows for a much broader choice of water-insoluble cofomers. Moreover, the reaction system could be kept under homogeneous conditions to avoid clogging the reactor. Indeed, hydrate nanocrystals that form from the water pools precipitate to the bottom of the reactor in the form of a slurry that is free-flowing and does not tend to clog (e.g., a discharge pipeline).

A hydrogen storage medium containing 1 wt %  $H_2$  and which can be stored in the freezer instead of being confined in very high pressure, Kevlar-coated metal canisters is more interesting than might be apparent.<sup>70</sup> According to a detailed comparison of the net energy content of several hydrogen storage media with hydrogen hydrates, a 1 wt %  $H_2$  content in hydrate provides approximately the same amount of net energy as a gas cylinder compressed at 20 MPa, whereas a clathrate hydrate filled with hydrogen at the theoretical limit (i.e., 5.6 wt %) has a higher net energy content than the current best performer, the 70 MPa cylinder.<sup>71</sup>

#### 4. FUTURE DIRECTIONS AND PERSPECTIVES

The reported studies highlight only some of the countless uses of surfactants. Nevertheless, they evidenced the strategies used by different authors and our research group to investigate in detail surfactant structure optimization in order to promote adsorption onto hydrophobic surfaces and to promote or inhibit the formation of clathrate hydrates, clarifying the prevailing interactions that drive these processes. This feature article is therefore intended to stress the fact that surfactants are not simply molecules that tend to self-assemble but rather molecules that, thanks to their amphipathic features and balanced hydrophilic/hydrophobic ratio, may be profitably used for a wide variety of applications. It is noteworthy that all of these properties are strictly bound to weak interactions such as van der Waals,  $\pi$ – $\pi$ , cation– $\pi$ , electrostatic, and solvophobic interactions where molecules are associated physically but not chemically. By modulating these interactions, it is possible to tune the surfactant behavior in order to favor self-assembly or adsorption onto a hydrophobic surface or the dissolution of elected materials or to favor/disfavor gas hydrate formation.



**Figure 7.** (A) SEM micrograph and (B) TEM micrograph of a lyophilized 5 gel sample. (C) SEM micrograph of a lyophilized gel sample of 5-coated MWCNTs. (D) SEM micrograph and (E) freeze–fracture SEM micrograph of a lyophilized gel sample of 5-coated MWCNT enriched with  $Ru_4POM$ . The scale bar is 20  $\mu m$  in (A), 1  $\mu m$  in (B), 10  $\mu m$  in (C) and 1  $\mu m$  in the corresponding inset, 100  $\mu m$  in (D), and 2  $\mu m$  in (E). Adapted with permission from ref 75. Copyright 2013, Wiley.



The features of widely used or newly synthesized surfactants are countless, and working on weak interactions, exploiting the amphipathicity of molecules, and taking advantage of their capacity to self-assemble will pave the way for future studies in a wide range of fields, not excluding very applicative sectors. For example, we have already investigated the ability of carbon nanotubes to act as a doxorubicin (DOX) carrier once coated with biocompatible PEG44-PPS20 block copolymers.<sup>72</sup> The major drawback of carbon nanotubes is the metal impurities connected with their preparation and responsible for the majority of their toxicity, once CNTs are well dispersed in solution.<sup>73</sup> We have great expectations for the study of graphene-enriched biomaterials in regenerative medicine and tissue engineering as evident in current investigations that exploit the biocompatibility of graphene<sup>53</sup> and graphene oxide and the capacity of biocompatible surfactants or liposomes to disperse graphene, thus allowing its adsorption onto different materials used in dental surgery such as hydroxyapatite and collagen membranes.<sup>74</sup> It could be interesting to exploit the capacity of some of the investigated ammonium surfactants to form gels. Recently we succeeded (Figure 7) in immobilizing negatively charged electrocatalyst ruthenium polyoxometalate (Ru<sub>4</sub>POM) at the elected loading onto noncovalently functionalized ammonium-derived CNTs and prepared a CNT-Ru<sub>4</sub>POM oxygen-evolving supramolecular complex that could be profitably used for water oxidation.<sup>75</sup>

Further works in progress relate to the passivation of metal and plastic surfaces of gas pipelines with graphene oligolayers in an attempt to prevent hydrate adhesion and the use of selective amphiphiles to enhance the hydrate-driven separation of CO<sub>2</sub> from CH<sub>4</sub> in biogas.

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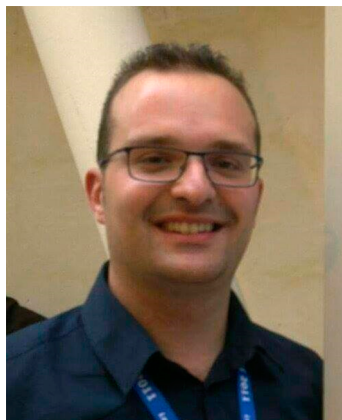
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### Notes

The authors declare no competing financial interest.

### Biographies



Antonello Di Crescenzo received his Laurea degree with honors in chemistry and pharmaceutical technology in 2007 and his Ph.D. (Doctor Europaeus) in pharmaceutical sciences in 2010 from the University "G. D'Annunzio" of Chieti under the supervision of Professor

Paolo De Maria. As a visiting scientist, he worked in the Laboratory for Regenerative Medicine & Pharmacobiology at the EPFL of Lausanne during 2008 (supervisor Professor Jeffrey A. Hubbell) and in the School of Chemistry and Centre for Research on Adaptive Nanostructures and Nanodevices at the Trinity College Dublin during 2010 (supervisor Dr. Silvia Giordani). Since 2011, he has had a postdoctoral position in the Laboratory of Organic Chemistry at the University of Chieti under the supervision of Professor Antonella Fontana. His research interests focus mainly on the preparation and characterization of carbon-based nanohybrid materials for application in the energy and biomedical field.



Pietro Di Profio received his Ph.D. in organic chemistry from the University of Perugia, working on modeling of the reactivity of micellar-associated reactions in water. He also worked as a visiting researcher in the laboratories of Prof. Clifford A. Bunton at the University of California, Santa Barbara, and Dr. David Nicoli, PSSNicom, on the implementation of algorithms for the application of dynamic light scattering to zwitterionic colloids. His major research topic is currently in the field of gas hydrates, particularly as relates to the effects of amphiphilic compounds on the inhibition or promotion of clathrate hydrates of methane, hydrogen, and carbon dioxide.



Gabriella Siani graduated in pharmaceutical chemistry at the University of Bologna, Italy, in 1991. She is an assistant professor of organic chemistry in the Department of Pharmacy at the University "G. d'Annunzio" in Chieti. Her scientific interests are mainly directed towards physical organic chemistry, and her main research fields are (1) solvent effects of nonconventional organic solvents on the thermodynamics and kinetics of organic reactions and (2) supramolecular chemistry: morphological and kinetic characterization of supramolecular aggregates (micelles and vesicles).



Romina Zappacosta, after obtaining a degree in chemistry and pharmaceutical technologies at the University of Chieti, Italy, earned her Ph.D. in pharmaceutical sciences at the same university. She is currently a postdoctoral research fellow in organic chemistry in the Department of Pharmacy of the University "G. d'Annunzio", Chieti, Italy. Her main field of interest is the supramolecular aggregation of natural and synthetic surfactants, with a special focus on the liposome stability, targeting, and capacity to entrap different guests. Recently, she studied the role of electromagnetic radiation in the processes of induction and/or the prevention of methane hydrate formation.



Antonella Fontana received her Ph.D in pharmaceutical sciences from the University of Bologna and is now associate professor at the University "G. d'Annunzio" of Chieti-Pescara. During her Ph.D., she worked on the thermodynamics, kinetics, and metal catalysis of tautomerization with Prof. R. M. O'Ferrall in Dublin. On study-leave from the University of Chieti, she worked on the kinetics of formation and breakdown of vesicles from natural (liposomes) and synthetic surfactants with Prof. B. H. Robinson at UEA in Norwich (U.K.) and Prof. D. Needham at Duke University in Durham, North Carolina (U.S.). Research areas of interest include the thermodynamics and kinetics of organic reactions in water, organic solvents, and nonconventional solvents; metal and micellar catalysis; physicochemical characterization of aggregates from natural (liposomes) and synthetic surfactants; dispersion and exfoliation of carbon-based systems; preparation of hybrid composite materials with carbon nanotubes and graphene for applications in catalysis, drug delivery, and artificial photosynthesis as well as the biosensor, biomedical, and energy storage fields.

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## ABBREVIATIONS

CPP, critical packing parameter; CNTs, carbon nanotubes; SWCNTs, single-walled carbon nanotubes; SDS, sodium dodecyl sulfate; NaDDBS, sodium dodecyl benzenesulfonate; SC, sodium cholate; PAH, polycyclic aromatic hydrocarbons; Triton X-100, 4-(1,1,3,3-tetramethylbutyl)phenyl-polyethylene glycol; IL, ionic liquid; MD, molecular dynamics; PEG-PPS, diblock poly(ethylene glycol-*bl*-propylene sulfide) copolymer; Pluronic, poly(ethylene glycol-*bl*-propylene oxide); ED, essential dynamics; DTAB, dodecyl trimethylammonium bromide; CTAB, cetyltrimethylammonium bromide; POPC, 1-palmitoyl-2-oleoylphosphatidylcholine; AFM, atomic force microscopy; CP, cyclopentane; THT, tetrahydrothiophene; THF, tetrahydrofuran; LDHs, low-dosage hydrate inhibitors; AAs, antiagglomerants; SL, sodium laurate; SO, sodium oleate; DBSA, 4-dodecylbenzenesulfonic acid; DAHC, dodecylamine hydrochloride; DTAC, dodecyltrimethylammonium chloride

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