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Influence of the hydrocarbon chain length of imidazolium-based ionic liquid on the dispersion and stabilization of double-walled carbon nanotubes in water

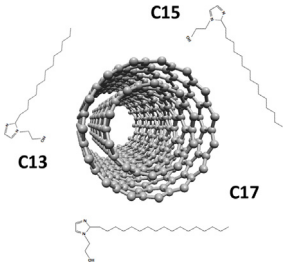
Kenza Raiah[a], Abdelkader Djalab[a], Amel Hadj-Ziane-Zafour[a], Brigitte Soula[b], Anne-Marie Galibert[b], Emmanuel Flahaut[b,c,*]

[a] Laboratoire de Génie Chimique, Université Saad Dahlab, Route de Soumaa, B.P. 270 Blida, Algeria
[b] Université de Toulouse, UPS, INP, Institut Carnot Cirimat, 118, Route de Narbonne, F-31062 Toulouse cedex 9, France
[c] CNRS, Institut Carnot Cirimat, F-31062 Toulouse, France

HIGHLIGHTS

- Synthesis of imidazolium-based ionic liquids from natural compounds (fatty acids).
- Stabilization of 50 mg/L double walled carbon nanotubes in water up to 20 days.
- Dispersibility increased with increasing the length of the hydrocarbon chain.

GRAPHICAL ABSTRACT



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ABSTRACT

Imidazolium-based ionic liquids with a long hydrocarbon chain 1-methyl-1-ethanol-2-alkyl-imidazolium iodide ([M-E-C_n-Im] I, n = 13, 15 and 17) were used for the dispersion of DWCNTs in water. DWCNTs suspensions obtained were stable for more than a month, and no sedimentation was observed. The stability of the suspensions was investigated (measurement of optical density, zeta potential, particle size, viscosity, and TEM images). Monitoring of the absorbance by UV/vis spectrophotometry for 20 days showed that at low concentration (1 mM), the best suspension was obtained with the ionic liquid ([M-E-C_{15}-Im] I). At higher concentration (10 mM), the dispersion efficiency increased with the length of the hydrocarbon chain. This could be explained by the hydrophobic interaction between the hydrophobic moieties of the ionic liquid and the CNTs. Therefore, we were able to stabilize DWCNTs using a low concentration (1 mM) of imidazolium-based ionic liquids synthesized from natural compounds. This work highlights the potential of imidazolium-based ionic liquids for the preparation of aqueous suspensions of DWCNTs at high concentration with a limited amount of added surfactant (50 mg/L of DWCNTs with 50 mg/L of ionic liquid).

1. Introduction

Carbon nanotubes (CNTs), described as such for the first time in 1991, are still of great interest for the scientific community due to their exceptional intrinsic properties (electrical, mechanical and thermal), opening a very wide field of applications for these

* Corresponding author at: CNRS, Institut Carnot Cirimat, F-31062 Toulouse, France. Tel.: +33 561556280.
E-mail address: flahaut@chimie.ups-tlse.fr (E. Flahaut).

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nanomaterials [1–3]. Though carbon nanotubes have promising applications, their insolubility in water and most organic solvents is challenging. This insolubility is explained by both intrinsic hydrophobicity and their strong agglomeration caused by van der Waals interactions and entanglement [4]. Several studies have tried to solve this problem by covalent functionalization methods [5–7] or by adsorption of amphiphilic agents [8–12]. Covalent functionalization using oxidizing acids at high temperature causes defects on the walls of the carbon nanotubes and their length decreases, therefore their electrical and mechanical properties are degraded [13,14]. Non-covalent functionalization by adsorption of surfactant or polymers and use of mild ultrasonic treatments, centrifugation and filtration does not disturb the π–π stacking or the lengths of CNTs, thus, maintaining intrinsic properties of the CNTs [15–17].

Different kinds of surfactants have been used successfully for the dispersion of CNTs, such as the anionic SDS (sodium dodecyl sulphate) [18,19], cationic CTAB (cetyl trimethyl ammonium bromide) [20,21] and non-ionic Triton X-100 [22]. However the nature of the surfactant and its concentration have an important role in the dispersion of CNTs in water and organic media [23,24]. Previous work has shown that ionic liquids have a better dispersing efficiency compared to conventional surfactants [25–28]. Some studies have been conducted on imidazolium-based ionic liquids: Kim et al. [29] prepared stable suspensions using an imidazolium-based ionic liquid (1-butyl-3-methylimidazolium tetrafluoroborate) and SWCNTs. SWCNTs suspended by imidazolium-based ionic liquid form a gel, called Bucky gel [30]. Non-covalent functionalization of oxidized single-walled carbon nanotubes by poly imidazolium-based ionic liquids was also used for the synthesis of gels [31]. SWCNTs dispersed in imidazolium-based ionic liquids [32] have been used as cathode in high-power lithium batteries. A MWCNTs suspension with 1-ethyl-3methylimidazolium tetrafluoroborate in dimethlformamide was used as an immunosensor of myeloperoxidase detection in human serum [33]. A magnetically sensitive material was prepared with SWCNTs and a magnetic ionic liquid (1-butyl-3-methylimdazolium [$FeCl_4$]), which finds applications in biomedical research (such as targeted drug delivery and controlled release, protein separation, cancer treatment) [34]. A method was developed to decorate MWCNTs with noble metal particles (gold) by the means of ionic liquid 1-hexadecyl-3-methylimidazolium bromide [27]. Yang et al. [35] performed a quantitative characterization by UV/vis spectrophotometry of SWCNTs suspensions prepared in ionic liquid 1-N-butylmethylimidazolium hexafluorophosphate.

Di Crescenzo et al. [26] have shown that the ionic liquid with a long hydrocarbon chain 1-hexadecyl-3-vinyl-imidazolium bromide formed a stable homogeneous aqueous dispersions with SWCNTs above its critical micelle concentration. Liu et al. [25] reported that they obtained stable aqueous suspensions of MWCNTs with ionic liquid-type Gemini imidazolium ([C_n-C_4-C_n-Im] Br_2, n = 12, 14) even at low concentration (1 mM). The binary mixture of 1-tetradecyl-3-methylimidazolium chloride/ethylammonium nitrate successfully dispersed MWCNTs [36]. The ionic liquid with polycyclic aromatic fraction and a long hydrocarbon chain – [n-(N-carbazole) alkyl]-3-methylimidazolium bromide yielded good CNTs suspensions in water (10 months, at 1 mM), showing the combined effects of both a hydrocarbon chain and a carbazole moiety [37]. The adsorption of the imidazolium-based ionic liquid onto SWCNTs was explained by their interaction with low van der Walls forces. Therefore, the electronic properties of SWCNT remained unmodified [38]. Madria et al. [39] have shown that 1-methyl-3-alkoxyalkyl and 1-methyl-3-fluoroalkyl imidazolium are relatively nontoxic to human health. Riduan et al. [40] investigated the use of imidazolium salts in several areas of bio-applications, including antitumor, antimicrobial, antioxidant and bioengineering. Imidazolium ionic liquids can be regarded as chemical compounds exhibiting a potential, slight toxicity to the growth and development of the early developmental stages of higher land plants [41]. Ionic liquids produced from the bio compounds choline and amino acids were found to have low toxicity to humans and to the environment [42].

In this context, the goal of this work was to disperse and stabilize DWCNTs in water, using imidazolium-based ionic liquids synthesized from natural material namely fatty acids. We investigated the ability of 1-methyl-1-ethanol-2-alkyl-imidazoline iodide to disperse the DWCNT, as well as the effect of the length of the hydrocarbon chain and concentration. In order to compare the efficiency of the three synthesized ionic liquids we monitored the concentration of CNTs versus time (optical density measurements); we measured the values of zeta potential and viscosity and also used static light diffusion to estimate the size of agglomerates. Finally, transmission electron microscopy observations were also performed in order to evidence de-bundling in the presence of surfactant.

2. Materials and methods

2.1. Materials

Double-walled carbon nanotubes (DWCNT) were synthesized at the CIRIMAT by catalytic chemical vapour deposition (CCVD) [43]. After extraction by treatment with a concentrated HCl aqueous solution (removal of catalyst support and unprotected metal nanoparticles), the CNT were recovered, washed and kept in a small volume of deionized water. The DWCNT thus prepared are called “raw wet tubes”. Myristic acid (99%), palmitic acid (99%) and stearic acid (99%), N (2-hydroxyethyl) ethylene diamine, ethyl iodide, were purchased from Sigma–Aldrich.

2.2. Synthesis and characterization of ionic liquids

Imidazolium-based ionic liquids ([M-E-C_n-Im] I, n = 13, 15 or 17) were synthesized by the reaction between the corresponding natural fatty acid with N (2-hydroxyethyl) ethylene diamine (Fig. 1). All the reagents were in the same molar ratio. The mixture was heated in toluene for 8 h with stirring and the water formed was removed azeotropically using a Dean–Stark apparatus. Resulting product was cooled and filtered and the solvent evaporated. The solid was precipitated by adding 1-butanol and then recrystallized from ethanol. The precipitated solid and ethyl iodide were heated by refluxing in isopropanol for 4 h, the resulting product was filtered and the solvent evaporated. The solid was precipitated by adding petroleum ether [44,45]. We obtained a good yield (91.5%) in agreement with those already published ((89%) [46], (92.1%) [44]). The characterization of the synthesized products was carried out by FT-IR, GC–MS, ^{1}H NMR and ^{13}C NMR analysis, and by measurement of CMC (critical micelle concentration).

The Fourier transmission infra-red (FT-IR) measurements were made on Perkin Elmer Spectrometer operating with UATR (Universal attenuation total reflectance), spectral range between 4000 and 650 cm^{-1}, at 4 cm^{-1} of resolution. The gas chromatography coupled with mass spectrometry (GC–MS) analysis was performed with a Perkin Elmer Clarus 500, RTX-5MS equipped with a capillary GC column (60 m, 0.25 mm, 0.25 μm), and the system was heated from 100 to 290 °C with a heating rate of 8 °C/min and kept at 290 °C for 10 min. The temperature of the injector and detector were 250 °C and 200 °C, respectively. The characterizations by ^{1}H NMR and ^{13}C NMR were carried out using a Brüker advance (500 MHz) equipped with a TCI probe type (Triple Cryoprobe Inverse); the samples were dissolved in $CDCl_3$. The determination of the critical micellar