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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

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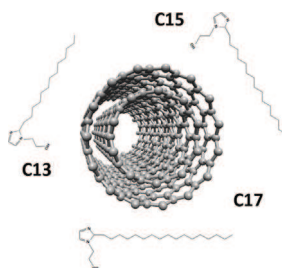
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HIGHLIGHTS

- 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



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-C₁₅-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).

Keywords:

Carbon nanotubes
Imidazolium-based ionic liquids
Aqueous suspensions
Stabilization

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

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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-3-methylimidazolium tetrafluoroborate in dimethylformamide 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-methylimidazolium $[\text{FeCl}_4]$), 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 $[\text{C}_n\text{-C}_4\text{-C}_n\text{-Im}] \text{Br}_2$, $n = 12, 14$ 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 Waals 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-imidazolium 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 $[\text{M-E-C}_n\text{-Im}] \text{I}$, $n = 13, 15$ 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, ^1H 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 ^1H 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

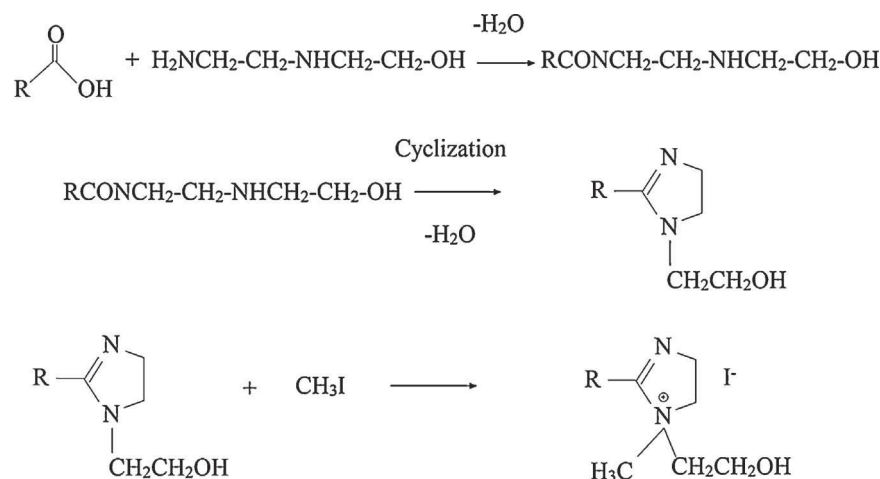


Fig. 1. General scheme for the synthesis reactions of the ionic liquids.

concentration (CMC) was performed by conductivity measurements (Hanna instruments, EC215).

The FT-IR spectra of the three ionic liquids are shown in Fig. 2. The presence of the band at 2922 cm^{-1} corresponds to CH_3 and CH_2 groups. The presence of a strong band at 3392 cm^{-1} indicates the formation of primary amine. In addition, the appearance of a band at 1642 cm^{-1} indicates the formation of the amide ($\text{C}=\text{N}$) and is an evidence of the formation of the imidazoline ring [46]. Mass spectra data were analysed using the NIST MS Search library, and the following spectral profiles were obtained with MS (m/z %): 74 (99), 84 (92), 87 (77), 43 (61), 56 (58), 44 (45), 128 (43), 41 (39), 55 (32) and 141 (26) (Fig. 3) [46].

The characterization by ^1H NMR has given the spectra show in Fig. 4. Identification of the peaks is: δ 3.04 ppm (t, 2H, $-\text{C}=\text{N}-\text{C}-\text{CH}_2-\text{N}-$), δ 3.38 ppm (t, 2H, $-\text{CH}_2-\text{C}-\text{OH}$), δ 3.71 ppm (t, 2H, $-\text{C}=\text{N}-\text{CH}_2-$), δ 2.21 ppm (t, 2H, $-\text{N}=\text{C}-\text{CH}_2-$). In Fig. 5 are shown the ^{13}C NMR spectra, indicating the presence of peaks δ 173.80 ppm ($-\text{N}=\text{C}-\text{N}-$) and δ 60.48 ppm ($-\text{C}-\text{OH}$). The main difference between the three spectra is around 3 ppm and corresponds to impurities (residues of reactants); the signals expected for our compounds are well identified, although ^1H NMR does not give any information about the aliphatic chain length.

Fig. 6 shows the variation of the electrical conductivity as a function of the concentration for the three ionic liquids. These curves allowed us to determine the values of the CMC for each ionic liquid. The CMC was close to 0.8 mM for the three compounds (the CMC is the concentration at which the slope changes, it was determined using the first derivative).

2.3. Dispersion of carbon nanotubes

DWCNT suspensions were prepared in deionized water alone. For each ionic liquid, a stock solution was also prepared in deionized water, under magnetic stirring for 4 h, in order to ensure the dissolution of each surfactant. The mixture of the two stock dispersion/solution (DWCNT and surfactant) was designed to obtain 10 ml suspensions of DWCNT at a concentration of 50 mg/L, and the three ionic liquids at concentrations equal to 1, 1.5 and 10 mM. DWCNT suspensions obtained were mixed in an ultrasonic bath (Bioblock T570, 35 KHz, 160 W) for 10 min, then using an ultrasonic probe (Vibra Cell Model 75 042, 20 kHz, 500 W) for 30 min at 25% amplitude with a pulse of 5 s on and 5 s off, in order to avoid overheating. Our choice of a high concentration of 50 mg/L is justified by further work related to the environmental impact assessment of such suspensions which will be required in order to compare the performance of these Imidazolium-based dispersing agents with

our earlier work with DWCNTs involving cellulose derivatives such as carboxymethylcellulose [47,48] or xanthan derivatives [17].

2.4. Characterization of suspensions

DWCNT suspensions were characterized by UV/vis absorption (Varian, Cary 300). The absorbance measurements were performed from 400 to 900 nm, immediately after preparation and following 20-day sedimentation. Zeta potential measurements were performed with zetasizer (Model ZEN 3691, Malvern Instruments), using suspensions centrifuged at 1600 rpm for 30 min. The supernatant was separated and then left to settle down for 24 h. No sedimentation could be observed within 24 h. The rate of viscosity versus shear rate was determined with a rheometer (Anton Paar Physica, Germany), operating with a concentric cylinder, and connected to a water bath in order to ensure a constant temperature of 25°C . Size measurements of dispersed colloids were performed by the technique of static light diffusion (SZ-100, Horiba Scientific), the sizes were measured for 48 h at regular time intervals. DWCNT suspensions were also characterized by transmission electron microscopy (JEOL 1400 TEM), operated at 120 kV. The samples were prepared by pipetting and dropping a few drops of suspension on 400 mesh Lacey Carbon copper grids, purchased from Agar Scientific.

3. Results and discussion

Characterization of DWCNT suspensions was performed by UV/vis spectrophotometry. Although individual CNTs may be UV-vis active in the measurement range (400–900 nm), there is no absorption band for bundled CNTs [12,25]. Fig. 7 represents the absorbance of the DWCNT suspensions at 50 mg/L with the three ionic liquids ($[\text{M}-\text{E}-\text{C}_n-\text{Im}]^+\text{I}^-$, $n = 13, 15$ and 17) at a concentration of 10 mM, as well as prepared in deionized water only (no surfactant). Although we did not observe any maximum absorbance band corresponding to CNTs, the effect of the addition of a surfactant was rather clear in terms of increased absorbance. As the ionic liquids do not have any absorption band within the analysed range, the absorption can only be attributed to CNTs.

The variation of the absorbance as a function of time (20 days) for the DWCNT suspensions prepared with the three ionic liquids at a molar concentration of 1 mM, 1.5 mM and 10 mM is shown in Fig. 8. The absorbance measurements were performed at 500 nm [22,49]. According to our data, at 1 and 1.5 mM concentrations, we obtained an almost identical absorbance with the two ionic liquids $[\text{M}-\text{E}-\text{C}_{15}-\text{Im}]^+\text{I}^-$ and $[\text{M}-\text{E}-\text{C}_{17}-\text{Im}]^+\text{I}^-$. The low concentrations (1 mM

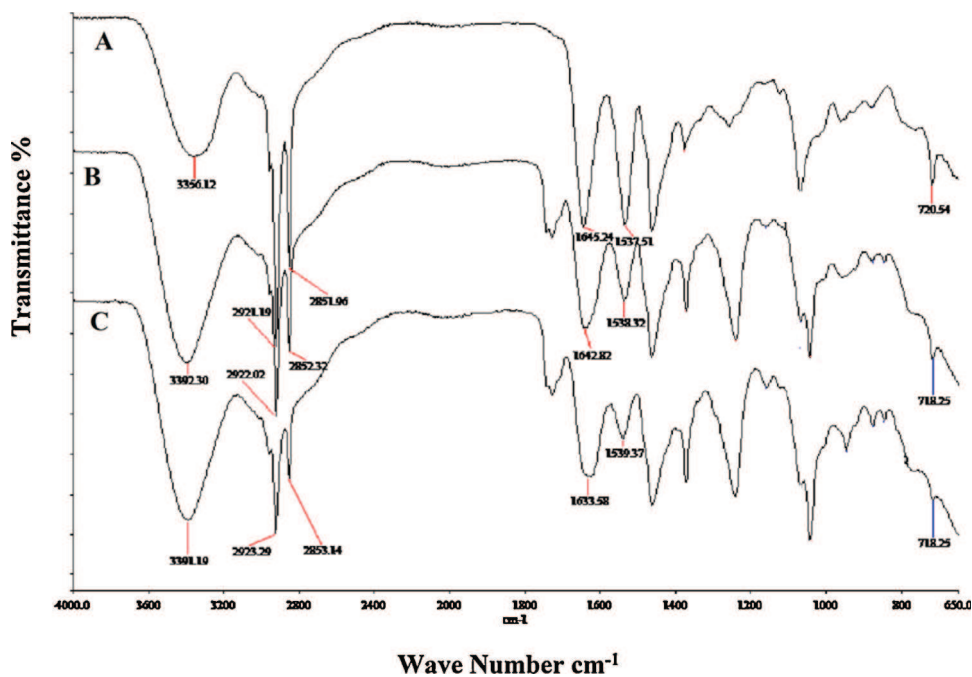


Fig. 2. FT-IR spectra of (A) [M-E-C₁₃-Im] I, (B) [M-E-C₁₅-Im] I and (C) [M-E-C₁₇-Im] I.

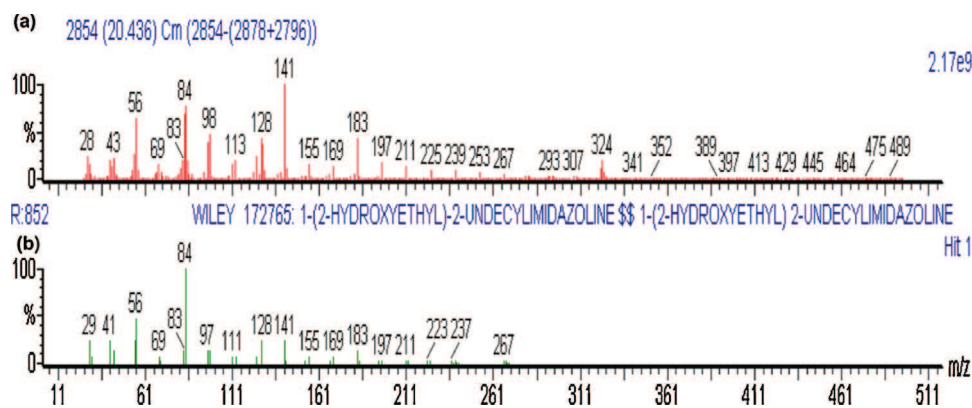


Fig. 3. Mass spectra of (a) [M-E-C₁₅-Im] I, compared to (b) data from NIST MS Search library (as an example).

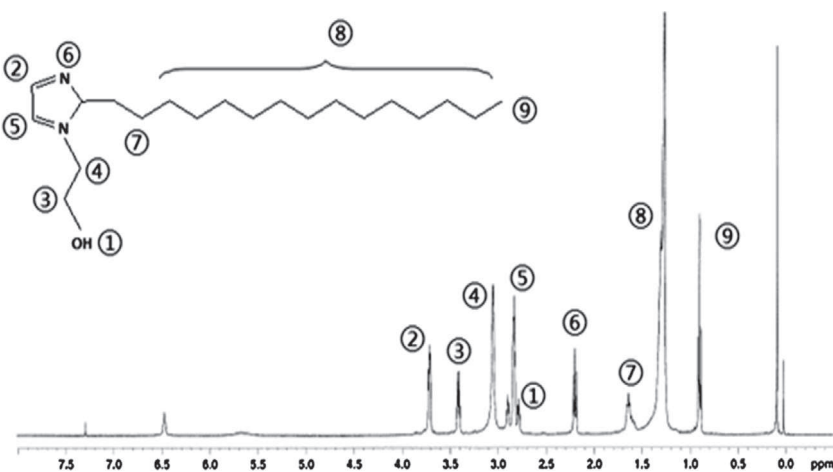


Fig. 4. ¹H NMR spectra of [M-E-C₁₅-Im] I (as an example).

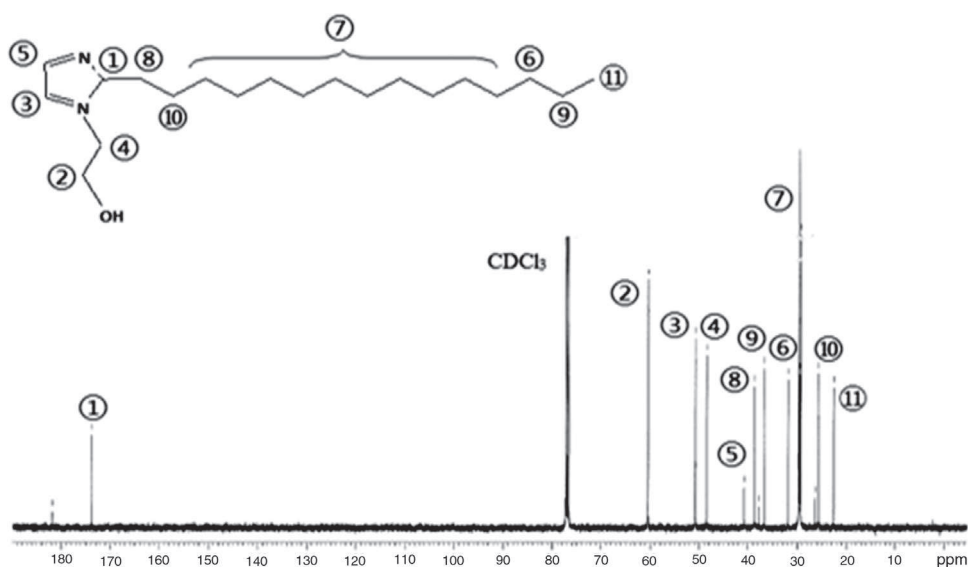


Fig. 5. ^{13}C NMR spectra of [M-E-C₁₅-Im] I (as an example).

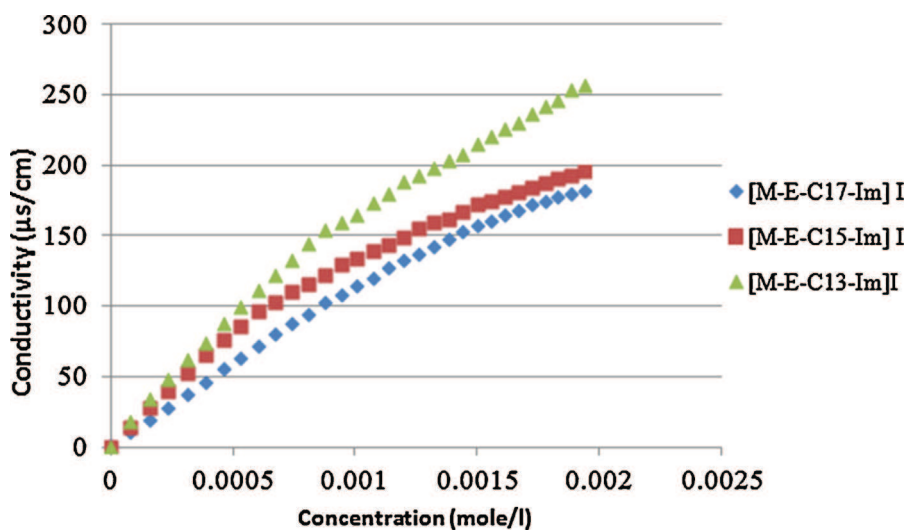


Fig. 6. Variation of the electrical conductivity as a function of the concentration of ionic liquid.

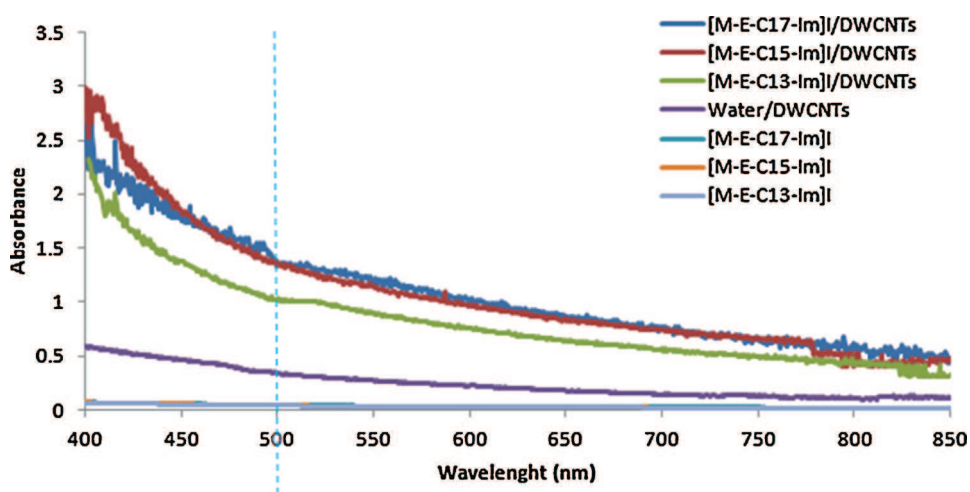


Fig. 7. UV/vis spectra of ionic liquids [M-E-C₁₃-Im] I, [M-E-C₁₅-Im] I, [M-E-C₁₇-Im] I at 10 mM and DWCNT suspensions with ionic liquids [M-E-C₁₃-Im] I, [M-E-C₁₅-Im] I, [M-E-C₁₇-Im] I and water only (immediately after preparation).

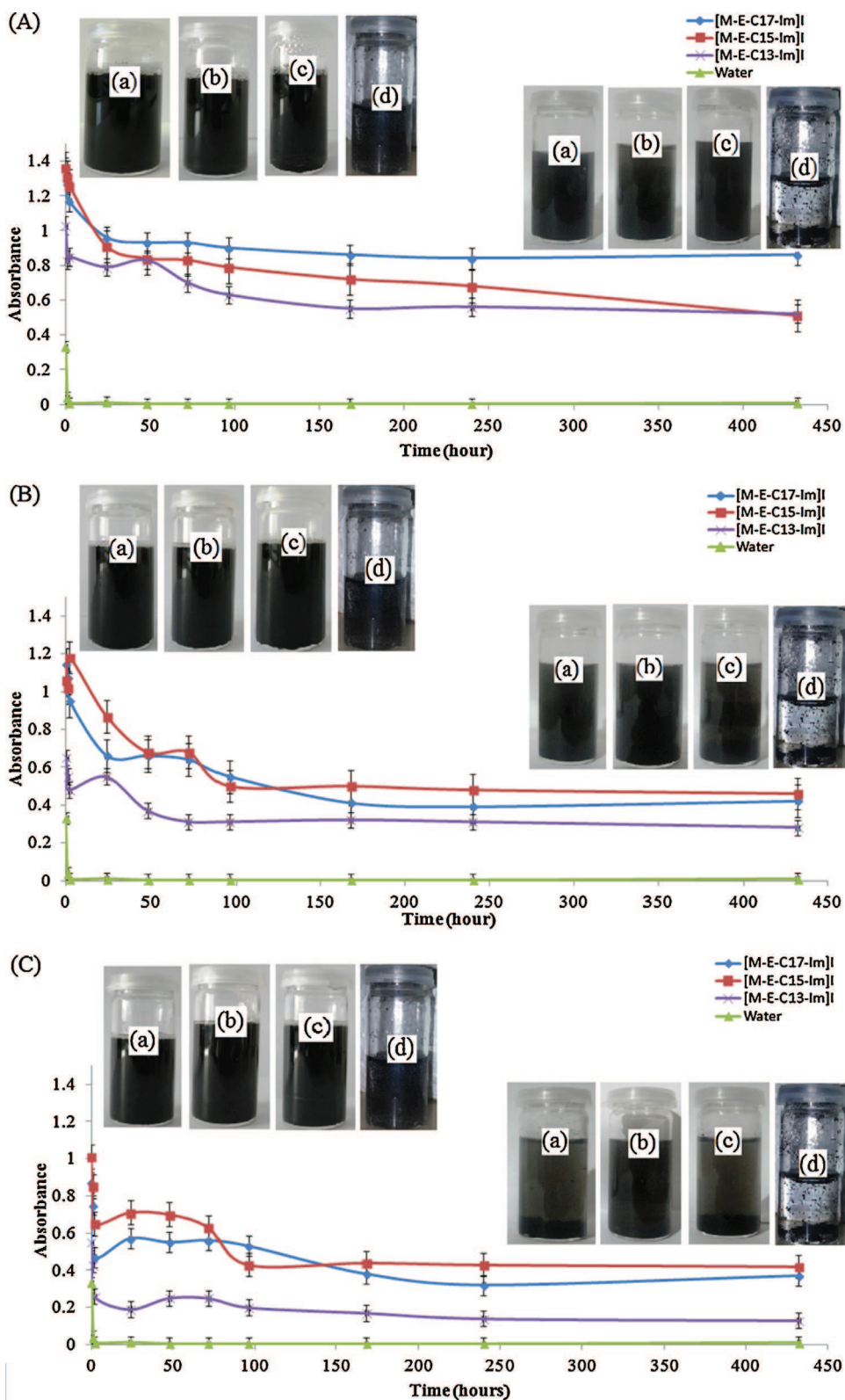


Fig. 8. UV/vis absorbance intensity versus time of DWCNTs (50 mg/L) in ionic liquids (a) [M-E-C₁₃-Im] I, (b) [M-E-C₁₅-Im] I, (c) [M-E-C₁₇-Im] I and (d) deionized water alone at a concentration of (A) 10 mM, (B) 1.5 mM and (C) 1 mM, up to 20 days.

and 1.5 mM) are just above the critical micelle concentration of the three ionic liquids (CMC is equal to ca. 0.8 mM, evaluated from electrical conductivity measurements) and did not lead to good dispersion and stability. This phenomenon can be explained by the fact that the dispersion of the nanotubes with the amphiphiles is only

possible above the limit of the CMC [50,51]. Thus, the dispersing power of the ionic liquids close to the CMC was low compared to the concentration of 10 mM (10 times more).

At the concentration of 10 mM of ionic liquid, the absorbance of suspensions increased with increasing the length of the

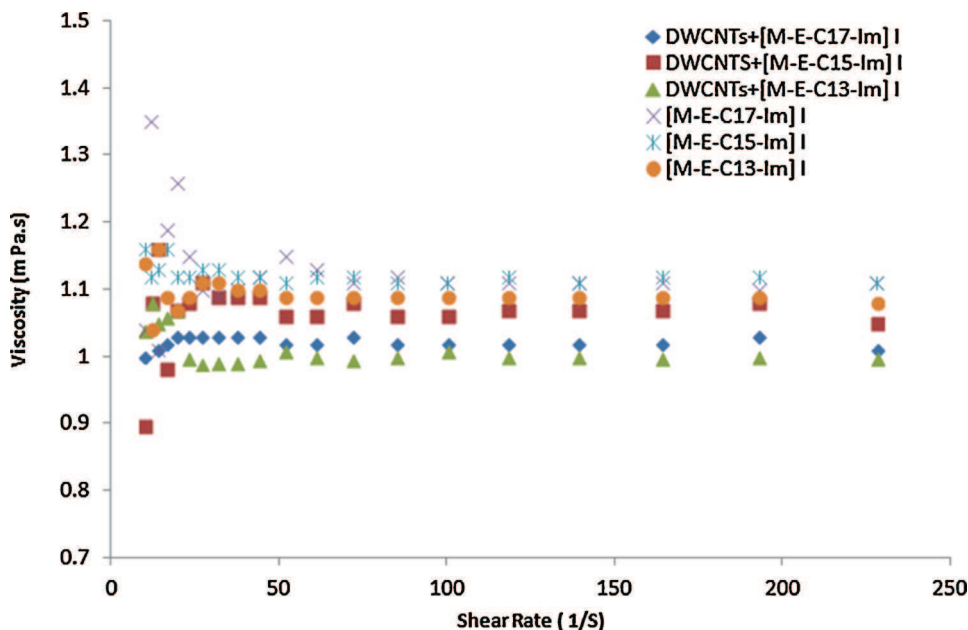


Fig. 9. Variation of the viscosity versus shear rate for the three ionic liquids of 1 mM and DWCNT (50 mg/L) suspensions with the three ionic liquids.

hydrophobic chain. The best value was obtained with the ionic liquid [M-E-C₁₇-Im] I. Similarly the absorbance of the suspension prepared with [ME-C₁₅-Im] I was higher than the one prepared with [ME-C₁₃-Im] I. The three ionic liquids have a homologous structure. The only difference lies in the length of the hydrocarbon chain (C = 13, 15 and 17). The increase in dispersing efficiency with increasing the length of the hydrocarbon chain can be explained by the increase in hydrophobic interaction between the hydrocarbon chains of ionic liquids and DWCNTs [25,52] (generally, because CNTs have a very hydrophobic surface, the hydrocarbon chains tend to be strongly adsorbed [53,54]). A better interface between the hydrophobic chain and the nanotubes means a higher stability of the adsorption and less possible exchanges with the surrounding solvent. In this comparison, there is probably no modification of the steric hindrance due to the small differences in terms of carbon atoms in the alkyl chain. Taking into account the fact that the charge is coming from exactly the same chemical group for the series of ionic liquids, the electrostatic repulsion is not expected to be different. If the difference in chain length was enough to lead to different rates of coverage onto the nanotubes, this should finally lead to a

different number of charges and this would finally be in favour of the shorter alkyl chain ionic liquid (C13). Consequently, we assume that the key parameter is the stability of the interaction between the adsorbed ionic liquid and the nanotubes, which is in favour of the longest alkyl chain.

The measurement of zeta potential is important to explain the stability of the colloidal particles in aqueous suspension [28,55]. We measured the zeta potential of DWCNT suspension using the three ionic liquids at the concentration of 1 mM and obtained zeta potential values larger than 40 mV. According to Dong et al. [37] the particles with a zeta potential larger than 15 mV in absolute value are considered to be stabilized by electrostatic repulsions. A high positive value of zeta potential indicates the strong adsorption of the ionic liquid to the surface of DWCNTs, leading to stable suspensions due to Coulomb force between the CNTs [25]. Therefore, a high stability of DWCNT suspensions was evidenced. Table 1 illustrates the values of zeta potential of the DWCNT suspensions with the three ionic liquids. The largest value of zeta potential was obtained with the DWCNTs suspension prepared with the ionic liquid [M-E-C₁₅-Im] I, although it is quite similar to the value obtained for

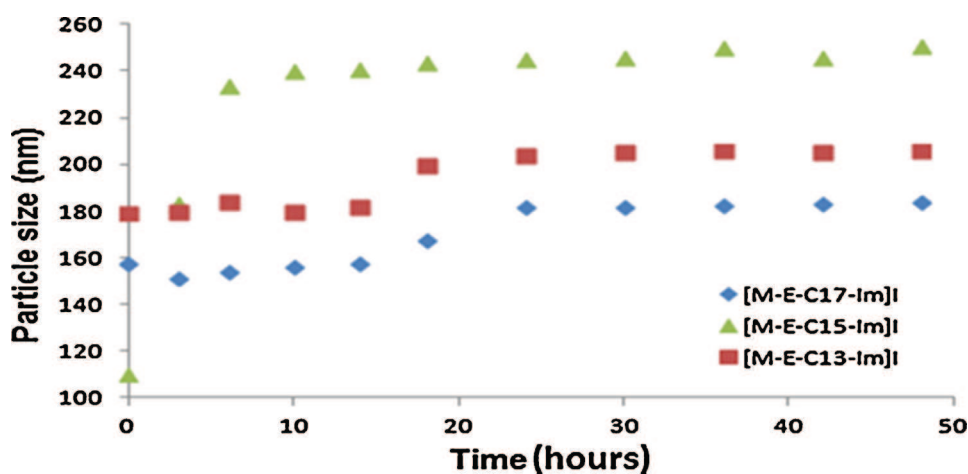


Fig. 10. Particle size of DWCNTs suspensions at 50 mg/L for the three ionic liquids at 1 mM.

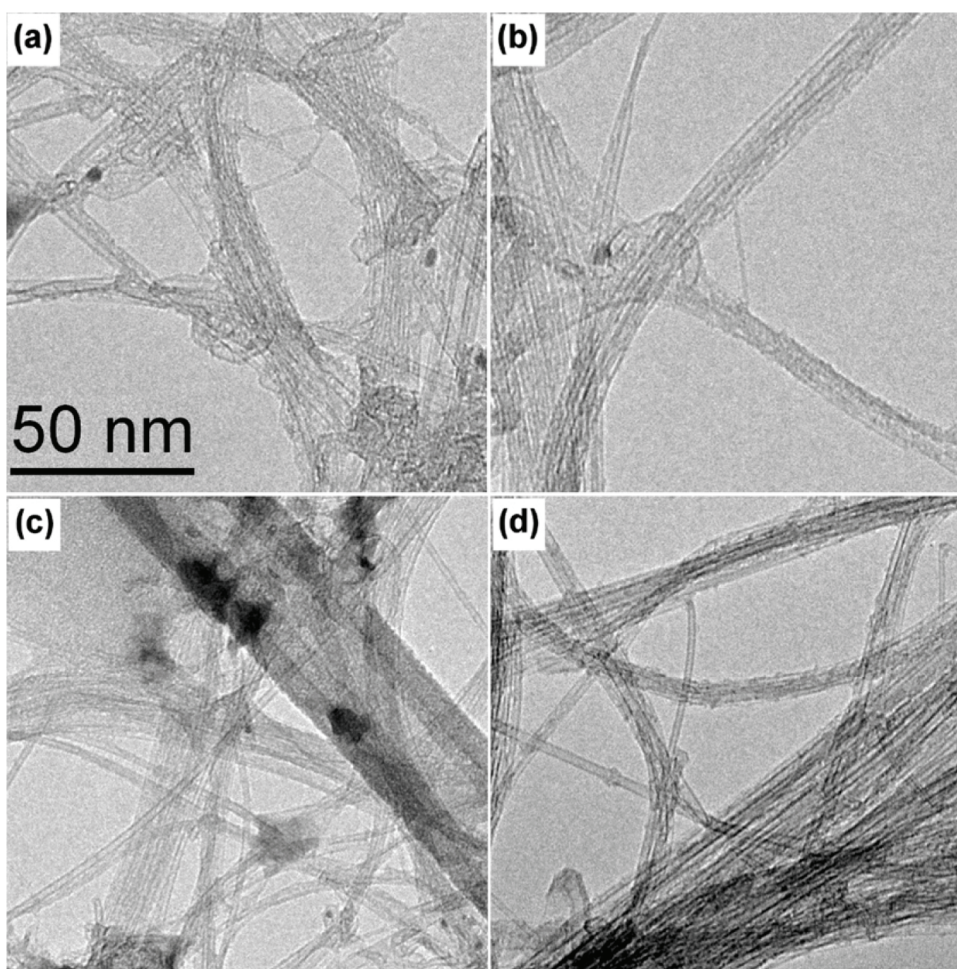


Fig. 11. TEM micrograph of DWCNT suspensions in deionized water at 50 mg/L with ionic liquid at 1 mM (a) [M-E-C₁₃-Im] I, (b) [M-E-C₁₅-Im] I, (c) [M-E-C₁₇-Im] I and (d) deionized water alone. The scale bar (50 nm) is identical for all four images (same magnification).

Table 1
Zeta potential of DWCNT suspensions for the three ionic liquids (1 mM).

DWCNT suspensions with ionic liquid	Zeta potential (mV)
[M-E-C ₁₇ -Im] I	60.6
[M-E-C ₁₅ -Im] I	66.0
[M-E-C ₁₃ -Im] I	45.0

[M-E-C₁₇-Im] I. These values are however significantly higher than the zeta potential measured for [M-E-C₁₃-Im] I in the same experimental conditions.

We were able to stabilize 50 mg/L of DWCNTs using a 50 mg/L of imidazolium-based ionic liquids compared to using 1000 mg/L of ionic liquid-type Gemini imidazolium for suspending 200 mg/L of MWCNTs [25].

The variation of the viscosity versus shear rate for the three ionic liquids and the DWCNT suspensions with the three ionic liquids is shown in Fig. 9. We have observed a low viscosity of the DWCNT suspensions with the three ionic liquids; this low viscosity can be explained by better charge repulsion between hydrophobic groups (the hydrocarbon chains) oriented along CNTs, when the hydrophilic heads are directed towards the aqueous phase, which prevents the agglomeration of the CNT [17,56,57].

In order to demonstrate the stability through time of the DWCNT suspensions, size measurements of dispersed colloids were performed by the technique of static light diffusion. For this purpose, suspensions of carbon nanotubes were prepared with the three

ionic liquids at 1 mM as stabilizers. The sizes were measured for 48 h at regular time intervals (Fig. 10).

Measurements of particle size for the three suspensions of DWCNTs with each ionic liquid clearly show that CNTs are in the form of very small agglomerates with an average diameter between 150 and 250 nm. We measured monomodal particle size distributions and a polydispersity index of 0.068 (the value of this index gives information about monodisperse systems, for which the index should be between 0.05 and 0.08). The size of the agglomerates in the suspensions of DWCNTs was practically stable during the 48 h of measurement and especially after 20 h.

Transmission electron microscope (JEOL 1400) images of DWCNTs suspensions prepared with three ionic liquids, as well as the ones prepared with deionized water alone, are shown in Fig. 11. These images show that the three DWCNTs samples stabilized by ionic liquids formed smaller bundles compared to DWCNTs in deionized water alone. Therefore, the use of ionic liquids limited the agglomeration of DWCNTs. However, it is important to note that TEM observations were performed after drying the samples on TEM grids, so the images are probably not showing the real situation in the suspensions in the presence of liquid (agglomeration upon drying during sample preparation).

Finally, DWCNTs have a morphology very close to SWCNTs and share with them the ability to form long and flexible bundles. In our DWCNTs samples, the bundles are not very large (typically 20–30 nm maximum) and the samples contain many individual (or at least individual part of their length). However, they are the first

multi-walled carbon nanotubes of the series and thus also share with larger MWCNTs the fact that the outer wall protects all the inner ones. As the interaction with a surfactant molecule is taking place only at the interface, the outer wall is the only to be concerned. DWCNTs are thus at the frontier between SWCNTs and MWCNTs in general and for this reason we can expect that the results of this study can be extrapolated to all other kinds of CNTs, as long as they are from bundles (which is still the case for many kinds of MWCNTs). However, it is clear that results may not be extrapolated to much shorter and individual CNTs, which could occur either intentionally if cutting procedures are applied (SWCNTs) or even unintentionally in the case of too strong sonication conditions for most MWCNTs.

4. Conclusion

Imidazolium-based ionic liquids 1-methyl-(1-ethanol)-2-alkylimidazoline ([M-E-C_n-Im] I, *n* = 13, 15 and 17) were synthesized from the corresponding natural fatty acids and shown to be able to effectively suspend carbon nanotubes in water, even at very low concentration (1 mM), for a period of more than a month. Quality of suspension was evidenced by optical density measurement, of zeta potential, particle size and TEM. The results of these analyses evidenced that we obtained stable suspensions, and also managed to partially de-bundle the DWCNTs. Comparing the dispersing strength of the three ionic liquids, we found that the dispersibility increased with increasing the length of the hydrocarbon chain, which is explained by the increased hydrophobic interactions between the hydrocarbon chain and DWCNTs. In addition, the suspensions of DWCNTs with ionic liquids had a viscosity similar to that of water, which is suitable for interaction with biological environments. Moreover, these results encourage the suspension of DWCNTs using imidazolium-based ionic liquids, for possible application in the study of toxicity/ecotoxicity of carbon nanotubes, thanks to their expected low intrinsic toxicity (which is however still to be measured for our series of new compounds). Acknowledgments

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