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Carboxylated carbon nanotubes corked with tetraalkylammonium cations: A concept of nanocarriers in aqueous solutions[☆]

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Abstract

An explicit water molecular dynamics simulations were used to probe (6,6) and (9,9) single-walled carbon nanotubes, functionalized with three carboxylate ion groups at each of the two openings, as potential nanocarriers in aqueous solutions. Three tetraalkylammonium cations (i.e., tetraethyl-, tetrapropyl-, and tetrabutylammonium) were tested as corks to cap the nanotube openings. The variation of the sizes of the nanotubes (diameter) and of the cork cations (bulkiness) allowed us to select the proper corks that fit the nanotube openings best. Smaller tetraalkylammonium ions could easily fit the openings, but since they are less hydrophobic compared to their larger analogues they showed less affinity for the interior of the nanotubes. On the other hand, the hydrophobicity (and thus the affinity for the nanotubes) can be adjusted through the increase of tetraalkylammonium cation size, providing that the cork still fits the opening. Additionally, an external electric field was tested as a means of nanotube uncorking. The field is capable of disjoining corked ions from the functionalized nanotube openings, triggering in this way a potential cargo release stored inside the nanotubes.

Graphical abstract

[☆]In honour of Prof. L. Blum.

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Appendix A. Supplementary data. Hydration effects of the CNT and TAA, seen through the CNT-water and TAA-water RDFs.

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Keywords

molecular dynamics; functionalized carbon nanotube; nanocarrier; tetraalkylammonium ions

1. Introduction

It is argued that carbon nanotubes (CNTs) were first discovered by Radushkevich and Lukyanovich in 1952 [1]. However, it was only recently that a paper by Iijima in 1991 [2] set fire to an increased interest in CNTs, inspiring further avalanche of studies of their properties and applications. The Scopus database reports counts of around 10,000 papers yearly dealing with CNTs. The main feature of CNTs, making them highly popular among other carbon allotropes, is the ultimately large ratio between their surface area and mass. Nowadays CNTs find their applications in a broad areas of science and technology [3]. Naturally, major attention is focused on CNTs in aqueous media and microscopic modeling of carbon-water interactions is therefore one of the top priorities in this area. One has to mention a series of molecular dynamics (MD) studies aimed to develop and utilize pair potentials for these systems [4–7].

Structural, dynamic and thermodynamic properties of water molecules inside CNTs were examined, for example, in Refs. [8–21]. A wetting mechanism of a dry CNT caused by the proton charge defect near the CNT opening was explored by Peng et al. [22]. A variety of CNT properties were also inspected, ranging from Young's modulus [23] and tensile strength [24] to electronic structures [25] and heat conductivity [26]. Carbon-based membranes were proposed for ethanol-water separation in Ref. [27]. Similarly, a MD simulations by Garate and Perez-Acle [28] have shown a high methanol and ethanol affinity to CNT pores, which in future could be used in the development of partitioning nanodevices. Freezing of water in CNTs exposed to an external electric fields was reported in Refs. [29–31], moreover, a variation of CNT chirality induces different ordering of water molecules.

Besides mechanical, electric, and thermal properties, chemical aspects are also of a special importance. Pristine carbon nanotubes are hydrophobic, while the most important factor varying their properties is the chemical functionalization: functional groups attached to CNT

walls extend the range of potential applications by changing their chemical nature or by decreasing their hydrophobicity. A precise control over positions and concentrations of functional groups at the nanotube surface is an experimental challenge. However, it has been concluded experimentally and theoretically that single-walled CNTs are more susceptible of being functionalized on the tips or vacancy defect sites [32–35]. A change of water ordering inside a CNT with $-\text{COOH}$, $-\text{C}=\text{O}$, and $-\text{CH}_3$ groups was explored by MD simulations in Refs. [5, 11, 12]. Proton dissociation and transfer dynamics in CNT functionalized with fluorosulfonic acid studied by *ab initio* MD was reported in Ref. [36]. Density-functional calculations of electronic properties of a CNT functionalized with $-\text{COOH}$ were reported by Zhao *et al.* [37]. Another study investigated the uranyl binding to a $-\text{COO}$ functionalized CNT [38]. An experimental study of uranyl adsorption from aqueous solution utilized amine functionalized CNTs [39], while Atieh *et al.* used oxidized CNTs as Pb complexants in their study of Pb removal from water [40]. The functionalization for ion selectivity or desalination phenomena were further exploited with oxidized CNTs [41, 42] and amino-doped graphene membranes [43, 44]. The phenomena of ion screening, hydration or selectivity in pristine CNTs were also explored in Refs. [45–49]. A nanotube confinement alters the hydration structure of Li^+ , Na^+ , and K^+ cations to a higher degree, rather than the hydration of F^- and Cl^- anions [45], while the CNTs of different size are used for ion selectivity between sodium and potassium [46]. The ion specific effects are also noticed by Beu [50] in the study of Na^+ , Cl^- , and I^- transport via nanopores.

A development of novel CNT-based adsorbents for detection or removal of toxic contaminants is another promising topic. Mechanisms of adsorption of radionuclides on CNTs are mostly related to a surface complexation and chemisorption of ions on CNT functional groups [51–54]. In particular, the nitrate adsorption on pristine CNTs is energetically favorable in the gas phase, but unfavorable in water due to a strong hydration of NO_3^- ions [55]. Carboxymethyl cellulose-CNT composites have shown an increased adsorption ability of uranyl from aqueous solution than unmodified CNTs [56]. Functional groups like $-\text{OH}$, $-\text{COO}^-$, $-\text{COOH}$, and $-\text{CONH}_2$ on CNT or graphene surface can serve as complexant spots for uranyl ions as reported by density-functional studies [38, 57]. Besides the complexation of simple ions, the CNTs are expected to be good adsorbents for longer molecules with hydrophobic parts [58–61]. Moreover, surfactants, if adsorbed on nanotube surface, can reduce its hydrophobicity by covering the surface with their hydrophilic groups [62, 63]. MD study conducted by Tummala and Striolo [62] have shown an aggregation of dodecyl sulfates on a graphite surface. Dodecyl sulfates are anionic surfactants with charged heads and hydrophobic tails, in particular, they were used for uranyl complexation in a series of studies [64–68]. Some other complexants for uranyls were considered in Refs. [69–72].

CNTs are also probed as nanocarriers: in particular, Ren and Pastorin [73] tested CNTs as a transport for cargo of hexamethylamine drug using fullerenes as corks. A study by Chaban *et al.* [74] suggested the idea of heat-stimulated release of drugs from CNTs. The drug release problem was also investigated in Refs. [75, 76], exploiting a pH-dependent behavior of functional groups. In Ref. [75] capping fullerenes were functionalized to achieve their release from nanotube openings at a certain pH, however, a further design was needed to adjust the triggering pH to the typical biological range for *in vivo* drug delivery. A technique

of pH-triggered drug release from oxidized CNTs was also reported in Ref. [76]. Indeed, the pH level is one of the simplest factors in charging CNT [41, 52] and enhancing surface complexation of adsorbates [40, 51, 77–79]. One has to mention a series of papers by Panczyk *et al.* [80–83] considering carbon nanotubes as nanocarriers for anticancer drugs cisplatin and doxorubicin with different corks (magnetic or golden nanoparticles) and release mechanisms (magnetic field or pH level). A MD study by Mejri *et al.* [84] modeled CNT as a cisplatin nanocarrier: the results showed that the cisplatin release was faster in near-membrane media compared to pure water. Functionalized carbon nanotubes were studied as potential nanocarriers for drug delivery to brain: *in vitro/vivo* experiments showed a reasonable uptake rates [85]. In parallel to carbon nanotubes the boron nitride (BNNT) ones were also probed as anticancer drug nanocarriers [86–89] with approximately same success. However, BNNTs are believed to have a few advantages: they are claimed to be less toxic than CNTs, and partial charges on B and N atoms polarize neighboring water molecules thus increasing BNNT's water permeation.

In this paper we discuss a concept of nanocarriers based on CNTs with anionic functional groups and tetraalkylammonium (TAA) cations acting as corks. The CNT uncorking and potential cargo release can be triggered by an external electric field. TAAs are chosen as example cations, however, this is not the only choice. CNTs and corks can be synthesized in a range of sizes, therefore, allowing to accommodate a variety of chemicals as cargo.

The remaining part of the paper consists of three sections. We present the model and simulation details in the section 2, the section 3 reports the results and discussion, followed by conclusions in the section 4.

2. Model and simulation details

Our model system mimics an aqueous solution of a functionalized CNT, having three COO^- groups attached at both openings, tetraalkylammonium (TAA) cations, and added Na^+ and Cl^- ions to assure for the charge neutrality of the system. The simulation cell includes water molecules explicitly.

Two different CNTs were utilized: (i) a (6,6) CNT with the diameter and length of about 8 Å and 20 Å, respectively, and (ii) a (9,9) CNT with these parameters being equal to about 12 Å and 20 Å. The stated diameters are average values and denote the diameter of the circle over the centres of carbon atoms composing the CNT openings. The length of CNT was chosen on two grounds: First, we wanted a tube that is longer than wider so that the events happening on one opening do not influence the interactions on the other side (short-range cut-off was 15 Å). Second, the length was also a compromise for the efficient computational time. Three COO^- functional groups were placed equidistantly on the carbon atoms of the CNT openings, at a separation distance of approximately 6.9 Å.

In addition to these two CNTs, three types of TAA cations were tested: tetraethylammonium (TEA), tetrapropylammonium (TPA), and tetrabutylammonium (TBA). All TAA ions, $[\text{H}(\text{CH}_2)_n]_4$ consisted of a central nitrogen atom tetrahedrally decorated with four alkyl “arms” ($n = 2, 3$ and 4 for TEA, TPA, and TBA, respectively; see Figure 1). Therefore, all

TAAAs bore the same nominal charge of +1 but differed in the length of the alkyl “arms”. The variation of TAA “size” (understood here as an increased bulkiness of the ion upon the increased length of the alkyl “arms”) changes the balance between the electrostatics and the hydrophobicity upon TAA-CNT interaction. Nominal diameters of the isolated TAA ions, σ_{TAA} , as a function of the alkyl chain length n can be calculated from their van der Waals volumes as $\sigma_{\text{TAA}}/\text{\AA} = 4.52 + 1.18n - 0.0612n^2$ [90]. For the TAA cations considered in this work, the estimated diameters are: 6.72 Å for TEA, 7.56 Å for TPA, and 8.26 Å for TBA. The “size” variation allowed us to identify which TAA cation fits the CNT openings best (i.e., can function as a best cork for the CNT). The corking of the CNT by TAA is here understood to be a consequence of either covering the CNT openings with TAA or by entering of the TAA into the CNT interior. Such design of the system is aimed to help docking the TAAAs and to further investigate how the exposure of the system to an external electric field can facilitate the disjointment of the TAAAs from the CNT openings (i.e., uncorking the CNT).

We generated a starting configurations consisting of 6300 water molecules, one functionalized carbon nanotube, CNT-(COO⁻)₆, six TAA cations, six Na⁺, and six Cl⁻ ions. The charges and the Lennard-Jones (LJ) parameters for sodium and chloride ions were taken from Ref. [91], the TAA parameters were taken from the OPLS force field [92], and water was described within the SPC/E water model [93]. The CNT-(COO⁻)₆ model was compiled from few sources: the charges and LJ parameters for carbons of nanotube sidewalls were taken from Ref. [5], C-C spring (bonds and angles) parameters were taken from the AMBER force field [94], while the LJ parameters, bonds and angles for carboxylate ion (–COO⁻) were the OPLS force field. We already used this set of parameters in our recent study [79]. All the parameters for the electrostatic and LJ interactions along with parameters for the intramolecular bond lengths and angles are collected in Tables 1, 2 and 3. The LJ parameters for unlike sites were calculated using the Lorentz-Berthelot mixing rules.

All particles were allowed to move freely within the cubic simulation cell box under the periodic boundary conditions. The cell sizes were 58 Å × 58 Å × 58 Å, assuring that the cell was large enough to accommodate the nanotube and to minimize the effects of self-interaction with the periodic replicas (see Figure 2).

All presented molecular dynamics (MD) simulations were performed using the DL POLY package [95]. In all the simulations we used the canonical NPT ensemble with the pressure of 1 bar and temperature of 298 K controlled by the Nose-Hoover barostat and thermostat in the Melchionna's implementation [96, 97]. The cut-off distance of 15 Å was chosen for the short-range interactions. The long-range Coulomb interactions were treated within the Ewald summation technique. The leapfrog algorithm was used for the integration of the equations of motion with a time step of 0.001 ps. The length of the production runs for different solutions ranged from 20 ns to 50 ns, except the length of the simulations with the applied external electric field where the simulations were 1 ns long (see below).

A set of three simulations for (6,6) CNT with TEA, TPA, and TBA cations was compared to the corresponding set of simulations for (9,9) CNT with TAAAs. The above comparison was intended to reveal which TAAAs were able to cork the CNTs. We also extended the (9,9) case

with three other simulations: instead of awaiting the corking event, we pre-deposited two of each TAAs inside the (9,9) CNT (see Fig. 3) and monitored the evolution of these systems.

Finally, in order to test the TAA ion release process, the three configurations of CNTs with pre-deposited TAAs were exposed to an external electric field. Three field strengths E were considered: (i) $0.05 \times 10^9 \text{ V m}^{-1}$, (ii) $0.5 \times 10^9 \text{ V m}^{-1}$, and (iii) $1.0 \times 10^9 \text{ V m}^{-1}$. The electric field was applied along the CNT axis. As a measure of the field effect we monitored in time relative coordinates of corking TAAs with respect to the CNT.

3. Results and Discussion

3.1. Interaction of TAAs with (6,6) and (9,9) CNTs, and with water

In this subsection we present the results of MD simulations of aqueous (SPC/E water) salt (Na^+ , Cl^-) solutions containing six TAA cations (TEA, TPA, or TBA) and one (6,6) or (9,9) CNT, functionalized with three $-\text{COO}^-$ groups at each of the openings. Initially, none of the TAA ions was located inside the CNT. Data are presented through various site-site radial distribution functions (RDFs).

During the course of the simulation we monitored the capability of TAA cations to cap the CNT openings. Over the whole simulation period none of TAAs entered the (6,6) CNT. The inability of the TAAs to enter the interior of the (6,6) CNT can be understood on the geometric grounds: the average inner diameter of the (6,6) CNT is approximately $4.5 \text{ \AA}$ which is too small to fit any of the TAAs (the diameter of isolated smallest TEA is $6.72 \text{ \AA}$). Contrary to the (6,6) case, we noticed the corking events of (9,9) CNT by TEA and TPA cations. In particular, one TEA entered (9,9) CNT after 4 ns and remained inside till the end of the simulation. Two TPAs entered (9,9) CNT, first at 6 ns and the second at 9 ns and remained inside the CNT for the rest of the simulation time. Therefore, the RDFs for the solution of (9,9) CNT with TEAs were averaged starting from 4 ns and onward, while the RDFs for (9,9) CNT with TPA were averaged starting from 9 ns of the production run and onward. The difference is rather quantitative than qualitative and does not change the overall conclusions. However, we wanted to stress this fact to exclude possible misinterpretations. TBA cations, compared to TEA and TPA, seem to be too large to fit the inner space of (9,9) CNTs, and no corking event was observed for these cations. The diameter of the isolated TBA is $8.26 \text{ \AA}$ while the average interior diameter of the (9,9) CNT is estimated to be approximately $8.5 \text{ \AA}$. Geometrically it is therefore unfavorable for the TBAs to enter the (9,9) CNT without substantial deformation of the CNT (see section 3.2). Even though none of the TAA cations entered the (6,6) CNT, we present these results along with the (9,9) ones for comparison purposes.

The RDFs describing the correlations between the (6,6) or (9,9) functionalized nanotube and TAAs are presented in Fig. 4. Panel 4a shows the RDFs between carbons belonging to CNT $-\text{COO}^-$ groups and nitrogens of TAAs ($\text{C}_{\text{COO}}-\text{N}$), panel 4b the RDFs between carbons of the CNT sidewalls and TAAs nitrogens ($\text{C}_{\text{CNT}}-\text{N}$), and panel 4c gives the RDFs between carbons of CNT sidewalls and carbons of trailing $-\text{CH}_3$ groups of TAAs ($\text{C}_{\text{CNT}}-\text{C}_{\text{TAA}}$). All graphs in Fig. 4 show unpronounced correlations between TAAs and (6,6) CNT. On the other hand, we see pronounced correlation peaks in the case of (9,9) CNT with TEA and

TPA cations. The correlations are the strongest in the case of TPA, reflecting our above conclusions that TPAs prefer to enter (9,9) CNT and remain inside the nanotube. Since TPAs fit the (9,9) CNT openings, one might think the smaller TEAs would even more easily enter the CNT, but as seen from Fig. 4 they rather show a moderate affinity to CNTs. Such result can be explained by TEA's relatively lower hydrophobicity (compared to other analogues with longer alkyl "arms"), favoring them to stay in the bulk and not entering the hydrophobic interior of the CNT. The maxima of main peaks of $C_{COO^-} - N$ RDFs for the solutions of (9,9) CNT with TEAs or TPAs are located in the range of 9-10 Å (cf. Fig. 4a). This is far beyond the distance of a direct contact, indicating that TEAs and TPAs pass the CNT openings and enter the CNT interior. The most hydrophobic and bulkiest TBA cations, instead, can not fit the CNT openings and therefore occupy the CNT outer sidewalls. $C_{CNT} - N$ RDF confirms this assumption: for TBA and (9,9) CNT one can see a relatively high and broad shoulder starting at 5 Å (cf. Fig. 4b). The RDFs between carbons of CNT sidewalls and carbons belonging to the trailing $-CH_3$ groups of TAAs (panel c of Fig. 4) agree with the conclusions made above – a distinct two-peak structure of the RDF in case of TEA and TPA solutions with (9,9) CNT corresponds to TAA cations trapped inside the nanotube. To remind, the (9,9) nanotube diameter is about 12 Å; this means that a $-CH_3$ carbon "sees" nearest CNT wall at a distance of ≈ 4 Å and diametrically opposite one at ≈ 8 Å. Such two-peak structure is not observed in cases where TAAs do not enter CNTs (i.e., TBA and (9,9) CNT, and all cases involving (6,6) CNT).

Let us next discuss the interaction of CNTs and TAAs with the ions of the added simple electrolyte, i.e. Na^+ and Cl^- . Sodium ions neutralize the charges of the CNT $-COO^-$ groups, and chloride ions compensate for the TAA cation charges. We show the RDFs between carbons of $-COO^-$ groups and Na^+ ions in Fig. 5a. A sharp first peak is located near 3 Å. There are additional two less pronounced peaks at ≈ 5 Å and 12 Å, as indicated in the inset of Fig. 5a. One can see that the first peaks for the (6,6) CNT cases dominate in magnitude over the corresponding peaks for the (9,9) CNT cases, i. e. the height of the first peak follows the trend (6,6) CNT + TEA > (9,9) CNT + TEA, and the same for TPA and TBA. We attribute this behavior to the fact that the charges on the (9,9) CNT openings are more screened by the docked TAAs compared to (6,6) CNT cases. Therefore, Na^+ ions lose the competition with TAAs and redistribute in the bulk solution. On Fig. 5b we present the RDFs between nitrogens of TAAs and chlorides. TEAs show an attractive first peak both in (6,6) and (9,9) CNT cases, while in the case of TPA and TBA the RDFs are weakly populated. Larger TPAs and TBAs show no correlation with chlorides.

The hydration features of the CNT and TAA cations are presented in the Supporting Information file. The population of water inside the CNT is low, while the $-COO^-$ groups are hydrated. The larger and more hydrophobic TAA cations avoid contacts with water by attaching themselves to the CNT side-walls.

By now, the reader has probably noticed that some of the presented RDFs in Figure 4 (and Figure 1 of the Supporting information file) do not approach unity within the range shown in the figures. This is not because of a numerical error but reflects the fact that elongated CNT keeps a certain degree of correlation even at longer distances.

3.2. Pre-deposited TAAs stay inside the CNT

This subsection summarizes the results of the study of the evolution of the aqueous system of CNT with some of the TAAs pre-deposited inside the nanotube. In addition to the above discussed simulation cases where at start of the simulation all the TAA cations were in the bulk solution, we performed a set of additional simulations of (9,9) CNT with two TAAs (of each type) pre-deposited inside the nanotube. Such a pre-deposition was aimed to reveal how different TAAs further behave inside the (9,9) CNT. All pre-deposited TAA ions remained inside CNT over the whole course of the simulation. However, a size-dependent behavior with respect to different TAAs was demonstrated. The best way to present this part of results is to discuss instantaneous configurations of the systems under investigation.

In Fig. 6 we show two projections of a given configuration of the nanotube with two pre-deposited TEAs. One can see that the TEA cations fit the nanotube interior well and are located close to the CNT openings. Other TEA cations are distributed in the bulk (and not seen in the snapshot).

A similar picture can be seen for the case of TPA cations in Fig. 7: they fit the inner cavity of the (9,9) CNT and locate close to the openings. Contrary to the TEA case, the positions of TPA nitrogens do not match the central axis of the CNT, since the more hydrophobic TPA alkyl “arms” try to cover CNT sidewall as much as it is allowed by TPA intramolecular bonds. One of TPAs also approached the outer sidewall of the CNT.

The nanotube geometry in both of the above examples (CNT with pre-deposited TEA and TPA) is close to a cylindrical one, which is not the case in systems containing TBA cations. In Fig. 8 the snapshots present the configuration of (9,9) CNT with two pre-deposited TBAs. One can see a substantial deformation of the CNT. This is because the estimated diameter of the van der Waals sphere representing the isolated TBA cation is almost the same as the average inner diameter of the (9,9) CNT. Despite the obvious distortion of the CNT the hydrophobic nature of TBA cations favors their stay inside the CNT. Moreover, a third TBA cation approaches the CNT opening and two more TBAs attach themselves to the outer sidewalls. Nevertheless, entering of TBAs inside the (9,9) CNT seems to be less realistic, as shown in systems without pre-deposited TBAs inside the CNT.

3.3. Uncorking effect of an applied external electric field

This subsection is intended to illustrate how CNTs, corked with different TAAs, behave when exposed to an external electric field of a given strength. It is expected that the electric field will reorient the nanotube along the field vector and disjoin the CNT and TAAs by pulling them in opposite directions. As a starting point we used three configurations of (9,9) CNTs with pre-deposited TEA, TPA, or TBA cations, as mentioned in subsection 3.2. Three field strengths E were probed: (i) $0.05 \times 10^9 \text{ V m}^{-1}$, (ii) $0.5 \times 10^9 \text{ V m}^{-1}$, and (iii) $1.0 \times 10^9 \text{ V m}^{-1}$, all applied along the Z -axis. In order to cut the computational overhead we chose the starting configurations with CNTs oriented close to the Z -axis. As a measure of the field's impact we monitored the longitudinal displacements of the pre-deposited TAAs within the CNT interior. In particular, the relative coordinates of TAA nitrogens were collected every 5 MD steps (0.005 ps) during a simulation lasting 1 ns. The time evolution of these

coordinates is collected in Fig. 9. We want to emphasize at this point that the tested strengths of the applied electric field are relatively high with respect to real aqueous solutions. However, for the rigid nonpolarizable water model used in this work, such electric field will not induce electrical discharge of the water molecules. Moreover, classical water models seem to underestimate the field effect (see, for example, Ref. [98] for the SPC/E and Ref. [99] for the CF1 water model, where it was shown that higher electric field compared to the experimental one needs to be applied to induce electrofreezing of water). We also want to stress that the field exposure in our simulation lasts only 1 ns. Such an interval can be considered as a nanopulse – short enough to make no discharge in real systems.

In Fig. 9a we compare the field influence on the release dynamics of TBA cations. An initial distance between nitrogens of corking TBAs was about 11.4 Å. The field of $1.0 \times 10^9 \text{ V m}^{-1}$ (denoted by blue lines) released TBAs at 7 ps and then at 200 ps. A twice weaker field of $0.5 \times 10^9 \text{ V m}^{-1}$ (green lines) releases TBAs on a slower rate: 80 ps and 800 ps, respectively. The first release at 80 ps was an extended event starting at ≈ 10 ps: a TBA cation approached CNT opening, but, apparently, it was being held by $-\text{COO}^-$ groups and, therefore, balanced on this position till 80 ps. The weakest considered field of $0.05 \times 10^9 \text{ V m}^{-1}$ (red lines) did not cause any release event during the 1 ns interval.

In Fig. 9b results for the TPA release dynamics are shown. According to this figure the initial distance between nitrogens of corking TPAs was ≈ 10.3 Å. The field of $1.0 \times 10^9 \text{ V m}^{-1}$ (blue lines) released TPA cations at 30 ps and 90 ps. The field of $0.5 \times 10^9 \text{ V m}^{-1}$ (green lines) released cations at 170 ps and 440 ps. Similar to the TBA case, the weakest field of $0.05 \times 10^9 \text{ V m}^{-1}$ (red lines) was not strong enough to release any TPAs within the 1 ns interval.

In Fig. 9c the time evolution of TEA coordinates is summarized. The initial distance between nitrogens of TEAs was ≈ 8.5 Å. The field of $1.0 \times 10^9 \text{ V m}^{-1}$ (blue lines) released TEAs at 14 ps and 110 ps. The second release consisted of two attempts: a cation approached CNT opening at ≈ 40 ps, went back, and finally leaved the CNT at 110 ps. The field of $0.5 \times 10^9 \text{ V m}^{-1}$ (green lines) released cations at a rather fast rate: 24 ps and 140 ps. Small and less hydrophobic TEAs were more easily released by both of these fields. Nevertheless, the weakest field – $0.05 \times 10^9 \text{ V m}^{-1}$ (red lines) – did not release the cations within the 1 ns interval.

The above results allow one to make few conclusions. First, the field makes a straightforward effect: the stronger the electric field the faster the TAA release. One can also assume that below a certain threshold field the TAA release is being blocked by a hydrophobicity of the TAA and its electrostatic attraction to CNT $-\text{COO}^-$ groups. As an aftermath, smaller in size TAA (less hydrophobic) can be released at a faster rate. However, we want to stress that in the current set of simulations, the initial positions of TBA, TPA, and TEA ions within CNTs were different, as well as the angles between the CNT and the *Z*-axis (i.e., the electric field direction). Therefore, one can fairly compare only the release dynamics of TAAs of a certain type with respect to the electric field strength. In order to compare the different TAAs, one has to conduct a series of samplings to average the mean

release times. More detailed estimates for the release times and threshold field strengths are beyond the scope of this study.

4. Conclusions

In this MD study we considered a concept of functionalized carbon nanotubes as potential nanocarriers in aqueous solutions. We used two types of CNTs: (6,6) and (9,9) ones, differing in the tube diameter. The openings of the CNTs were functionalized with --COO^- groups, while tetraalkylammonium cations were probed as corks. Since we do not know an optimal size of TAA cation in advance, three types of TAA cations were considered: TEA, TPA, and TBA. They all possess the same nominal charge of +1 but differ in “size” allowing one to choose the cation fitting the CNT openings best. The success of a TAA to aim a CNT opening is governed by a balance of various factors: (i) the --COO^- groups guide a TAA ion to the CNT openings, (ii) the larger the TAA (more hydrophobic) the more it tends to attach itself to the CNT outer and inner (if allowed by geometrical size) sidewalls, (iii) smaller TAA cations easily fit the CNT interior, but smaller TAAs are less hydrophobic. The simulations revealed that the (6,6) CNTs were too small to accommodate any of the tested TAAs, while slightly larger (9,9) CNTs were able to host TEA and TPA cations. We also conducted a series of simulations with initially pre-deposited TAA cations inside the (9,9) CNTs: two of TEA, TPA, or TBA cations were placed inside the nanotube at the beginning of the simulation. None of the pre-deposited TAA cations left the nanotube during the course of simulation, however, a noticeable deformation of the CNT in case of TBA cations was observed. The study was extended with a set of short simulations (1 ns each), where corked (9,9) CNTs were exposed to an external electric fields of different strength: $0.05 \times 10^9 \text{ V m}^{-1}$, $0.5 \times 10^9 \text{ V m}^{-1}$, and $1.0 \times 10^9 \text{ V m}^{-1}$. The field was expected to disjoin the anionic CNT and cationic corks. The results of this study imply that stronger electric fields make TAA release from CNT on a faster rate. Smaller and less hydrophobic TEAs are easily released, contrary to larger TBAs. The weakest field of $0.05 \times 10^9 \text{ V m}^{-1}$ did not cause the release of TAAs within the 1 ns interval. A threshold field for such systems is a factor preventing premature uncorking of a CNT and unwanted potential cargo release. In all the successive release events both corks moved in the same direction through the CNT: in a case of cargo release the corks will act as “pistons” helping to push out the cargo from the CNT. As a conclusion we assume that for the case of (9,9) CNTs the TPA cations seem to be optimal corks. As a final remark, one has to bear in mind that larger in diameter CNTs are able to accommodate larger (and more hydrophobic) TAA cations simply due to geometrical reason. Such a size play allows one to tune the process of CNT corking. In this way adjusting a threshold field strength allows one to trier the uncorking process.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Highlights

- Tetraalkylammonium ions can function as corks for carbon nanotubes - a potential nanocarrier system in water.
- Corking capability of tetraalkylammonium ions is a balance of their bulkiness and hydrophobicity.
- External electric field applied above a certain threshold strength functions as uncapping mechanism

Figure 1. Structural formulas of TAA cations together with the estimated values of the van der Waals diameters for isolated cation.

Figure 2.

A snapshot of a simulated solution containing a functionalized (6,6) CNT, TEA cations (depicted by sticks) and SPC/E water molecules (red-white wireframes). Na^+ and Cl^- ions are not shown. Carbons are shown in gray, oxygens in red, hydrogens in white, and nitrogens in blue. We see two TEA cations approaching a sidewall and the opening of the CNT.

Figure 3.
A snapshot of the simulated solution containing the (9,9) CNT with two pre-deposited TEA cations inside the nanotube. The color indication is the same as in Fig. 2.

Figure 4.

The RDFs between various sites of (6,6) and (9,9) CNT and TAAs. Panel a: carbons belonging to CNT --COO^- groups and nitrogens of TAAs, $g_{\text{COO-N}}$, panel b: carbons belonging to CNT sidewalls and nitrogens of TAAs, $g_{\text{CNT-N}}$, and panel c: carbons belonging to CNT sidewalls and carbons of trailing --CH_3 groups of TAAs, $g_{\text{COO-C}_{\text{TAA}}}$. Various cases are designated as indicated in the legend on panel a.

Figure 5.

Panel a: The RDFs between carbons belonging to -COO^- groups on the (6,6) and (9,9) CNT and Na^+ ions, $g_{\text{COO-Na}}$. Panel b: The RDFs between nitrogens of TAAs and Cl^- ions, g_{NCl} . Various cases are designated as indicated in the legend on panel a.

Figure 6. Two projections of a configuration taken after 40 ns of simulating an aqueous system containing (9,9) CNT with initially pre-deposited TEA cations. The color indication as in Fig. 2.

Figure 7.
Same as in Fig. 6, but for pre-deposited TPA cations.

Figure 8.
Same as in Fig. 6, but for pre-deposited TBA cations.

Figure 9.

Time evolution of the pre-deposited (a) TBA, (b) TPA, and (c) TEA relative coordinates within the (9,9) CNT. Three electric fields were considered: $0.05 \times 10^9 \text{ V m}^{-1}$ (red), $0.5 \times 10^9 \text{ V m}^{-1}$ (green), and $1.0 \times 10^9 \text{ V m}^{-1}$ (blue). The time axis is shown in a logarithmic scale.

Table 1

Coulomb (q) and Lennard-Jones (ϵ and σ) interaction potential parameters used in this work. C_1 in the TAA description belongs to CH_2 groups neighboring to nitrogen, C_3 belongs to terminal CH_3 groups, while C_2 hosts intermediate CH_2 groups (if present). The hydrogen type H_1 stands for atoms adjacent to C_1 , while H_2 denotes all other hydrogen atoms.

species	atom	q [e_0]	ϵ [kcal mol ⁻¹]	σ [Å]
H ₂ O	O	-0.8476	0.1554	3.1656
	H	0.4238	0.0	0.0
Cl ⁻	Cl	-1.0	0.1	4.4045
Na ⁺	Na	1.0	0.1	2.5865
TAA	N	0.0	0.17	3.25
	C ₁	0.19	0.066	3.50
	C ₂	-0.12	0.066	3.50
	C ₃	-0.18	0.066	3.50
	H ₁	0.03	0.03	2.50
	H ₂	0.06	0.03	2.50
CNT-COO ⁻	C	0.0	0.07	3.55
	C _{anchor}	-0.1	0.07	3.55
	C _{COO}	0.7	0.105	3.75
	O	-0.8	0.21	2.96

Table 2

Force constant (k_r) and the equilibrium bond-length (r_0) parameters of the harmonic potential form $k_r(r - r_0)^2/2$ used in this work to account for the valence bonds.

species	bond	k_r [kcal mol ⁻¹ Å ⁻²]	r_0 [Å]
TAA ⁺	N-C	734.0	1.471
	C-C	536.0	1.529
	C-H	680.0	1.09
CNT-COO ⁻	C-C	938.0	1.4
	C _{anchor} -C _{COO}	742.0	1.522
	C _{COO} -O	1312.0	1.25

Table 3

Force constant (k_θ) and the equilibrium bond-angle (θ_0) parameters of the harmonic potential form $k_\theta(\theta - \theta_0)^2/2$ used in this work to account for the valence angles.

species	angle	k_θ [kcal mol ⁻¹ deg ⁻²]	θ_0 [deg]
TAA ⁺	C–N–C	100.0	113.0
	N–C–C	160.0	111.2
	C–C–C	116.7	112.7
	H–C–H	66.0	107.8
CNT–COO [−]	C–C–C	0.03838	120.0
	O–C _{COO} –O	300.0	126.0