RSC Advances

RSCPublishing

ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Key Role of the Linker in Pyrene-Linker-Carboxylate Surfactants for the Efficient Aqueous Dispersion of Multiwalled Carbon Nanotubes

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This study establishes that the structure of the linker group between the hydrophobic and hydrophilic units in the new surfactants **1-13** plays an important role in the dispersibility of multiwalled carbon nanotubes (MWNTs) in water. Systematic variation of the linker group in amphiphilic surfactants for carbon nanotubes has not been previously investigated. In the present series, the hydrophobic unit is derived from pyrene, the hydrophilic unit comprises 1-9 carboxylate groups and the linker is based on amide or ether moieties. The resulting MWNT-surfactant dispersions, up to concentrations and efficiencies of ca. 160 mg L^{-1} and almost 50%, respectively, have been characterised by UV-Vis absorption spectroscopy studies which provide detailed structure-property relationships, while transmission electron microscopy (TEM) was used to confirm that the MWNTs were well dispersed. For many of the new surfactants enhanced dispersion efficiency is observed compared to commercial surfactants. The efficiency of dispersion is affected by the presence, functionality and particularly the length of the linker, and also the number of terminal carboxylate units. The marked effect of sodium, potassium and calcium cations on the dispersion behaviour is explained by interactions between the metal ions and the surfactant and an ionic screening mechanism. We also demonstrate that the dispersibility of the MWNT-surfactant dispersions can be reversibly switched 'off' and 'on' by addition of acid and base, respectively. The experimental results are supported by theoretical calculations of solvation energy ΔE_S. This study represents a significant advance in the design of multi-functional surfactants for efficient aqueous dispersion of carbon-based materials.

Introduction

The remarkable properties of carbon nanotubes (CNTs)[1-4] have led to a wide range of proposed academic and industrial applications within the field of nanotechnology and beyond: for example molecular wires and other materials for molecular electronics, sensors and probes, high-strength fibres and films, composites, biological electronic devices and hydrogen storage.[5] One obstacle limiting the use of CNTs is the difficulty in processing these materials,[6] which generally form tightly packed bundles due to strong inter-tube π-π and van der Waals interactions.[7] This results in an extremely low solubility in all common solvents (in the absence of additional functionalisation).[8] A common method of overcoming these forces is the use of surfactants[9,10,11] and other dispersants (e.g. polymers[12,13,14] or small molecules[15]) which can coat the highly hydrophobic surface of CNTs and disrupt attractive inter-tube interactions. Such non-covalantly functionalised CNTs can be dispersed in water and other solvents due to the improved miscibility imparted by the surfactant or dispersant. Efficient dispersion of CNTs requires energy input to allow surface functionalisation and debundling to occur, for example the use of ultrasonication.[6] Covalent functionalisation is an alternative means of improving the dispersibility of CNTs, but it has the disadvantage of disrupting their structure, which has a negative impact on many of their properties.[16-19] Non-covalent functionalisation is, therefore, preferable in applications which rely on the sp^2 structure of CNTs, with the further advantage that in some applications the dispersant can be removed from the CNTs after processing.[20]

The dispersion of CNTs in aqueous media[10,11] is of particular interest as water is both a "green" and readily available solvent. The pH and ionic strength of water are also easily adjusted, and both are known to influence the effectiveness of solvents at dispersing CNTs.[21] Better understanding the effects of these changes would allow for the design of improved surfactants, which could be used to prepare dispersions which respond to environmental stimuli. Such materials have potential applications as biosensors, purifying agents, catalysts or drug delivery vehicles.

Surfactants that efficiently disperse CNTs in water typically comprise an anchoring moiety which interacts strongly with a CNT surface through π-π interactions, and a hydrophilic head group to render surfactant-functionalised CNTs water miscible. Effective anchoring groups include polycyclic aromatic species such as anthracene,[22] pyrene,[7,23] perylene,[10,21,24,25] porphyrin derivatives[26] and more complex 'nanotweezer' systems.[27,28] Suitable hydrophilic moieties include carboxylate, ammonium and sulfonate salts,[9] polyethylene glycol (PEG) derivatives[23] and Newkome[7,21,24,27] and glycerol[25] dendrons. Crown ethers and podands based on short ethylene glycol oligomers (OEGs) can also be effective hydrophilic moieties.[29]

Most prior work in this field uses surfactants in which the anchoring and hydrophilic moieties are linked by the synthetically most convenient units, without consideration of the role this linker may play in CNT dispersion. We now present a systematic study which demonstrates that *variations in the linker unit significantly affect the ability of otherwise identical surfactants to disperse MWNTs in both low and high ionic strength media*. A computational investigation helps to rationalise these results and shows that the ability of a surfactant to disperse MWNTs can be related to its solvation energy ΔE_S. We also show that MWNT dispersions prepared using our new surfactants are destabilised at low pH but can be re-formed by neutralising the added acid. MWNTs were chosen for this study as they offer the advantages of relatively cheap large-scale production applicable for commercial applications.[30]

Results and discussion

Surfactant Design and Synthesis

The target surfactants incorporate one or more linker repeat units derived either from 6-aminohexanoic acid ('C6 linker') or ethylene glycol ('PEG linker'), i.e. linkers based on amide or ether functionalities, respectively (Figure 1). These hydrophilic linkers were selected to ensure that the surfactants were not too hydrophobic to act as dispersants. We have also investigated different hydrophilic head groups, as this has previously been shown to have an effect on CNT dispersing ability.[7] We have studied simple monocarboxylate head groups ('G0') and more complex moieties derived from first- and second-generation Newkome dendrons ('G1' and 'G2' respectively).[31,32] We selected a different dendron to that used by Hirsch's group,[7, 21] as the presence of ether oxygen atoms in the dendron branches could further enhance the hydrophilicity and CNT dispersing ability of the surfactants. In all of our molecules the anchor group was derived from pyrene (i.e. 1-pyrenebutyric acid or 1-pyrenebutanol). Pyrene derivatives offer both high binding affinity to CNTs[7,23,33,34,35] and synthetic versatility. Selected commercial surfactants*(structures in Figure 2) and 'linker-free' surfactants (**1** and **2** in Figure 1) with a head group bound directly to an anchor group were also investigated for comparison.

The C6 linker surfactants (**3** – **6**) were synthesized using iterative procedures, whereas for the PEG linker surfactants (**7** – **13**), commercially available OEGs allowed installation of the linker unit in a single step. Full details of the syntheses of the surfactants are given in the SI. The resulting library of molecules, including linker-free surfactants (**1** and **2**), is shown in Figure 1.

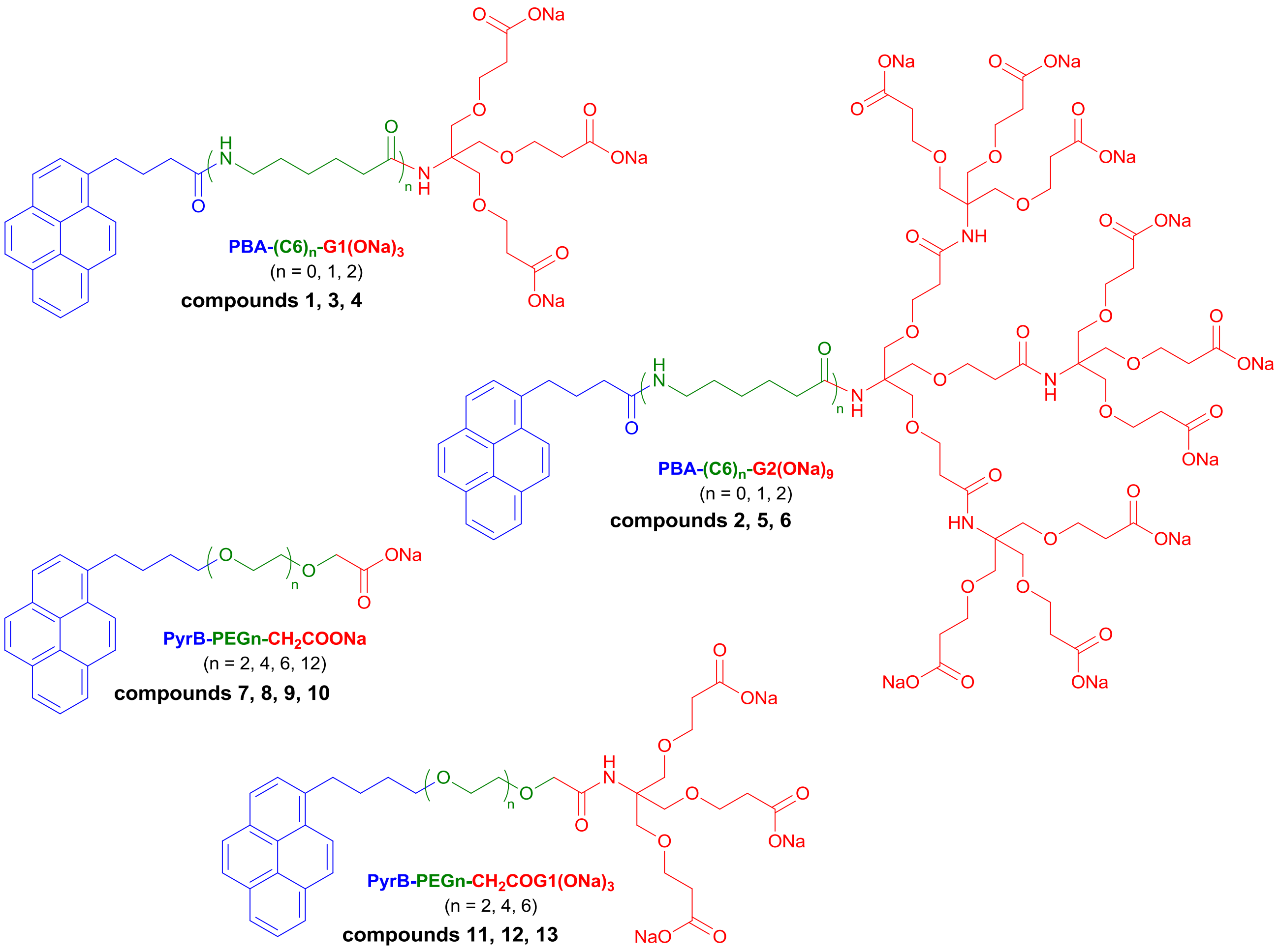

Fig. 1 The structures of the new surfactant compounds **1-13**, grouped according to the structure of the linker and the hydrophilic head group.

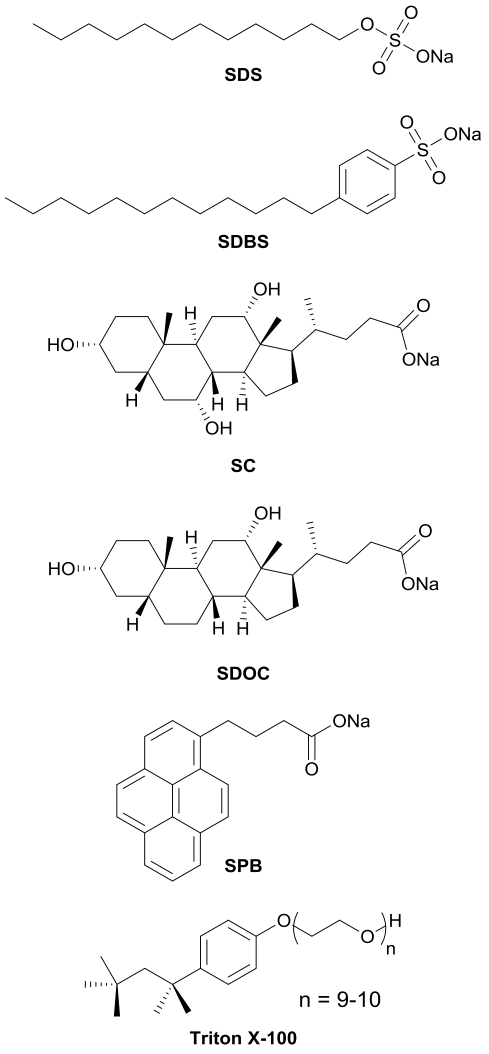

Fig 2 The structures of the commercial surfactants used for comparison purposes.

Preparation of MWNT Dispersions

We investigated the concentration of MWNTs (C_{MWNT}) in aqueous dispersions prepared using standardised conditions[29] (see SI), in either Millipore (DI) water or 0.6 M NaCl solution, using the new surfactants and compared their performance against several commercially available surfactants as references (Figure 3 and Table S1). All surfactants were investigated at the same 1 mM concentration, to allow comparisons to be made on a 'per molecule' basis. This concentration lies at the lower end of the range typically encountered in the literature, particularly for the commercial surfactants, but is comparable to the 0.5 g L^{-1} surfactant loading used by the Hirsch group for similar pyrene-based surfactants,[7] Optimisation of surfactant concentration was beyond the scope of this study, but we anticipate that improved performance could be achieved. The optimal concentration would, however, likely vary from molecule to molecule.[36, 37] C_{MWNT} was determined using the Beer-Lambert law with an apparent extinction coefficient (ε) of 49.9 ± 1.2 ml mg^{-1} cm^{-1} at 500 nm (see SI for details).[†] The MWNT dispersions are stable for at least several months under ambient conditions; they remain visibly homogeneous with no precipitation. Analysis of samples by transmission electron microscopy (TEM) confirmed that the MWNTs were well-dispersed and individualised (Figure 4). Some MWNT fragments smaller than the manufacturer's specified length range of 10-30 μm can be seen; however, partial fragmentation of CNTs is a known effect of ultrasonication. A recent study discusses methods by which this effect can be minimised.[38]

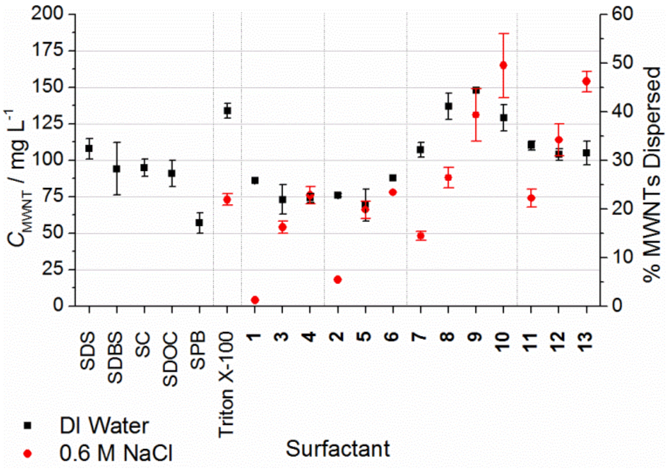

Fig 3 C_{MWNT} in a range of 1 mM surfactant solutions in Millipore (DI) water (black) and 0.6 M NaCl solution (red). Error bars are the standard deviation of at least 3 results except for **6** which represents a single experiment (due to the very small quantity of compound synthesized). The grey vertical lines separate surfactants into related groups, from left to right: commercial anionic, commercial non-ionic, linker-free and C6 linker G1, linker-free and C6 linker G2, PEG linker G0 and PEG linker G1.

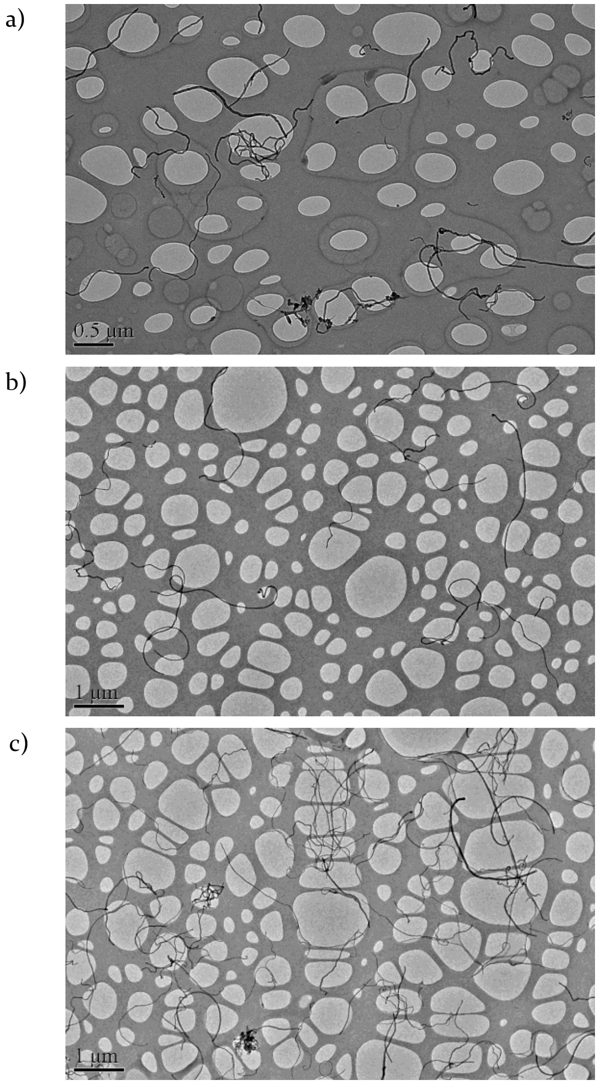

Fig 4 Representative TEM images on a holey-carbon grid of MWNTs dispersed using 1 mM surfactant solutions in DI water: a) **3**; b) **8**; c) **11**.

Dispersions in DI Water

Reference Commercial Surfactants: The commercial anionic surfactants **SDS**, **SDBS**, **SC** and **SDOC** dispersed similar levels of MWNTs (27-32%) under our standard conditions. **SPB** was less effective (only 17%). The strong π-interactions between the pyrene moiety and MWNT surfaces should ensure that the pyrene unit lies parallel to the CNT surface,[33] with a large molecular 'footprint.' This could, however, result in a lower CNT surface charge density compared to surfactants with aliphatic tails which can pack more efficiently in micelle-like or supramolecular structures.[24,39] The commercial non-ionic surfactant **Triton X-100** afforded a C_{MWNT} of 134 ± 5 mg L^{-1} (40%), which is considerably higher than any of the anionic species used as references. However, it should be noted that non-ionic surfactants achieve CNT dispersion through a combination of hydrophilicity and steric effects, rather than through charge interactions as in the case of ionic surfactants.[40]

*New pyrene surfactants **1-13**:* The linker-free and C6 linker surfactants (**1-6**) were slightly less efficient dispersants than the commercial anionic surfactants. This observation is comparable to the results of Backes *et al.* who obtained more concentrated dispersions of SWNTs using **SDS** than with surfactants similar to **1** and **2**.[7] The presence of one or two C6 linkers (compounds **3-6**) does not have a significant effect on C_{MWNT} under these conditions, nor does the choice of head group (i.e. G1 or G2). These results could also relate to the large footprint of the pyrene surfactants relative to **SDS**.

In contrast, in DI water the PEG linker surfactants (**7-13**) all gave C_{MWNT} levels at least comparable to the best-performing commercial anionic surfactant, **SDS**. They outperformed all of the linker-free and C6 linker species, indicating that the inclusion of the hydrophilic PEG linker enhances surfactant performance. This is exemplified by a comparison of the G0 series (**7-10**) with the linker-free analogue **SPB**, which was the least effective dispersant studied in this work, with a C_{MWNT} of only 57 ± 7 mg L^{-1} (17%). The addition of only three ethylene glycol repeat units to its structure gives **7**, which is almost twice as effective, with a C_{MWNT} of 107 ± 5 mg L^{-1} (32%). Extension of the PEG linker initially gives increases in C_{MWNT} [137 ± 9 mg L^{-1} (41%) for **8** and 148 ± 1 mg L^{-1} (44%) for **9**] but further extension is of no additional benefit [C_{MWNT} = 129 ± 9 mg L^{-1} (39%) for **10**].

The same trend is not observed for the G1 PEG linker surfactants (**11 - 13**), which all gave C_{MWNT} in the range 104-110 mg L^{-1} (31-33%), i.e. comparable to **SDS**. We attribute this to the difference between the G0 and G1 head groups; the latter will have a reduced surface packing efficiency due to increased Coulombic repulsions.[7] It is, however, again clear that the inclusion of a PEG linker is advantageous when the results are compared to the linker-free analogue **1** [C_{MWNT} = 86 ± 2 mg L^{-1} (26%)]. When compared to the G1 C6 linker surfactants (**3** and **4**), these data also demonstrate that the nature of the linker is important: the addition of a short PEG unit increases C_{MWNT} whereas addition of a short C6 linker causes a slight reduction in C_{MWNT}. The more hydrophilic PEG linker may allow the head group to extend further from the MWNT surface into the aqueous phase, which could give improved surface coverage and a smaller molecular footprint.

Dispersions in 0.6 M NaCl

To probe the effect of a high ionic strength medium on the ability of the surfactants to disperse MWNTs we prepared dispersions in 0.6 M NaCl solution. Note that this represents a much higher ionic strength than previous comparable studies of Hirsch *et al*,[21] meaning that charge screening effects are enhanced.

Most of the commercial reference surfactants were insufficiently soluble in 0.6 M NaCl to enable dispersions to be prepared under our standard conditions. However, a dispersion was obtained using 1 mM **Triton X-100** in 0.6 M NaCl, albeit with a C_{MWNT} only around half that obtained in DI water. This may relate to the effect of ions on the properties of **Triton X-100** micelles,[41] which are known to increase in size with increasing NaCl concentration. This suggests a reduction in hydrophilicity which will, in turn, impact on the ability of this surfactant to disperse MWNTs.

Screening Effect of the Ions: The presence of 0.6 M NaCl greatly reduces the ability of linker-free surfactants **1** and **2** to disperse MWNTs [C_{MWNT} of 4 mg L^{-1} (1%) and 18 mg L^{-1} (5%), respectively, in 0.6 M NaCl vs. 86 ± 2 mg L^{-1} (26%) and 76 ± 1 mg L^{-1} (23%), respectively, in DI water]. We attribute this to the screening effect of the dissolved ions (i.e. the reduction in the Debye length), which reduces the dispersive effect of Coulombic repulsion between surfactant-functionalized MWNTs. The higher C_{MWNT} obtained in 0.6 M NaCl for **2** compared to **1** reflects the higher charge on the G2 (vs. the G1) head group; a higher charge density will reduce the impact of ionic screening. The increase in charge screening should also reduce the effect of Coulombic repulsion on packing efficiency.[21] The extent of MWNT surface coverage by **1** and **2** is, therefore, expected to be more similar than in DI water.

Role of the Linker: Compared to the linker-free surfactants **1** and **2**, significantly higher levels of MWNT dispersion were achieved with the C6 linker surfactants (**3** – **6**) in 0.6 M NaCl. C_{MWNT} ranged from 54 ± 4 mg L^{-1} (16%) for **3** to 78 mg L^{-1} (23%) for **6**. The results for **1** – **6** contrast with those in DI water, where the linker-free surfactants generally gave a slightly higher C_{MWNT} than the analogous C6 linker species. It is clear from these data that the C6 linker plays a key role in facilitating MWNT dispersion in the presence of NaCl. Both C6 series (i.e. G1: **1**, **3**, **4**, and G2: **2**, **5**, **6**) show a large increase in C_{MWNT} when a single C6 linker is inserted (**3** and **5** vs. their respective linker-free analogues **1** and **2**) with a smaller increase on addition of a second C6 linker (**4** and **6**). For **4** – **6**, C_{MWNT} is comparable in both DI water and 0.6 M NaCl. We therefore propose that a favourable ion-dipole interaction between dissolved ions and the amide moieties in the linker improves the MWNT dispersing ability vs. linker-free species **1** and **2**. Although surfactants **1** and **2** each contain a single amide bond, it appears that any favourable ion-dipole interactions are not sufficient to overcome the negative effects of charge screening. Steric hindrance may play a role in reducing the effect of ion-dipole interactions in this case, as in **1** and **2** the amide moiety is in close proximity to both the quaternary carbon of the dendron and the pyrene moiety, whereas in **3** – **6** each amide is shielded by at most one of these groups.

PEG Linker Series: For the PEG linkers, both the G0 (**7** – **10**) and G1 (**11** – **13**) series show an increase in C_{MWNT} in 0.6 M NaCl with linker length, paralleling the trends observed for the two C6 linker series in 0.6 M NaCl and for the G0 PEG linker series in DI water. Unlike the C6 linker series, for some PEG linker surfactants C_{MWNT} is *higher* in 0.6 M NaCl than in DI water, in spite of the effect of ionic screening. Indeed, in 0.6 M NaCl, G0 surfactant **10** and G1 surfactant **13** gave the highest C_{MWNT} levels observed in this work [165 ± 22 mg L^{-1} (49%) and 154 ± 7 mg L^{-1} (46%), respectively].

Unlike in DI water, **10** gave a higher C_{MWNT} than its shorter-linker analogues (**7** - **9**) in 0.6 M NaCl. These results establish that the combination of a PEG linker and an ionic head group is important, as **Triton X-100**, which has a slightly shorter (average 9.5 repeat units) PEG chain but a non-ionic head group gives much lower C_{MWNT} in 0.6 M NaCl than in DI water. Similarly, structurally related *non-ionic* surfactants showed that 0.6 M NaCl significantly reduced C_{MWNT} compared to DI water.[29] The G0 surfactants with shorter PEG linkers, **7** and **8**, are both significantly less effective in 0.6 M NaCl, giving C_{MWNT} levels considerably lower than in DI water. The other member of the series, **9**, gives a level much closer to that obtained previously in DI water.

The G1 PEG linker series (**11** – **13**) includes a surfactant which is less effective in 0.6 M NaCl than in DI water (**11**), one which is very similar in both media (**12**) and one which shows a considerable improvement in 0.6 M NaCl (**13**). Clearly small variations in the linker unit can have a significant impact on the effect of ions on C_{MWNT}. Unlike in DI water, in 0.6 M NaCl the G1 surfactants consistently outperform their G0 analogues. This mirrors the results for the C6 linker species in 0.6 M NaCl, where G2 surfactants tend to give higher C_{MWNT} than their G1 analogues, and can be explained in the same way: the three anionic carboxylate moieties in a G1 head group mean the molecule is less adversely affected by ionic screening compared to a monocarboxylate G0 analogue. Improved surface coverage due to lower Coulombic repulsion between surfactant molecules may also play a role. Surfactants **11-13** all show a much higher C_{MWNT} than their linker-free analogue **1**, further highlighting the importance of the linker unit.

These trends are consistent with favourable interactions between ether oxygen atoms and sodium cations. Interactions between ions and amide moieties, as proposed for the C6 linker surfactants, are also possible in the case of G1 surfactants. We note that for both the G0 and G1 series, C_{MWNT} (in 0.6 M NaCl) appears to increase linearly with the number of PEG repeat units in the region n = 2-6 (i.e. **7-9** and **11-13**), and that the rate of this increase is similar for both series (~ 20 mg L^{-1} per PEG repeat unit). However, the trend is not continued with the longest PEG analogue **10**. Furthermore, linker-free **1** gives a slightly lower C_{MWNT} than extrapolation of this trend would predict, perhaps due to its more sterically hindered amide group.

Dispersions in Other Salt Solutions

Selected surfactants (**1**, **3**, **4**, **9** and **13**) were also tested for their ability to disperse MWNTs in the presence of 0.6 M KCl and 0.3 M $CaCl_2$ (Figure 5 and Table S2). 0.3 M $CaCl_2$ was used to maintain the same overall charge density as the other salt solutions.[‡]

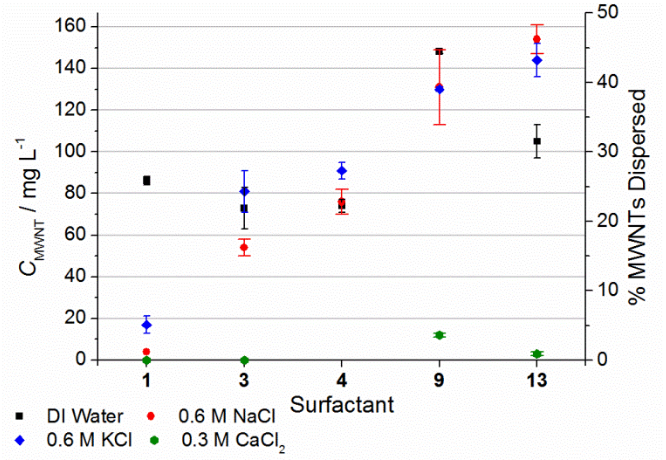

Fig 5 C_{MWNT} obtained using 1 mM solutions of selected surfactants in Millipore (DI) water (black), 0.6 M NaCl (red), 0.6 M KCl (blue) and 0.3 M $CaCl_2$ (green). Error bars are the standard deviation of 3 results.

The C_{MWNT} for **1** in 0.6 M KCl is significantly lower than in DI water [17 ± 4 mg L^{-1} *vs.* 86 ± 4 mg L^{-1} (5% *vs.* 26%)] but higher than in 0.6 M NaCl [4 mg L^{-1} (1%)]. Surfactants **3** and **4** both give a higher C_{MWNT} in 0.6 M KCl than in either DI water or 0.6 M NaCl. The same trend is seen along the series with both KCl and NaCl: a large increase in C_{MWNT} upon addition of the first C6 linker followed by a smaller increase upon addition of the second. These results fit our previous hypotheses. The ionic screening effect should be the same for both 0.6 M NaCl and KCl as equimolar solutions of 1:1 electrolytes have the same Debye length. Amides are known to interact slightly more favourably with potassium ions than with sodium ions due to their lower hydration enthalpy,[42,43] which may explain the observed increase in C_{MWNT} in 0.6 M KCl *vs.* NaCl. It appears that the cumulative effect of these slightly more favourable interactions with multiple amide groups induces a reasonably large change in C_{MWNT}. The increase in C_{MWNT} for **1** in 0.6 M KCl relative to 0.6 M NaCl indicates that ion-dipole interactions can occur despite the somewhat hindered amide moiety, but that they are still insufficient to overcome the adverse effect of ionic screening.

In 0.6 M KCl both **9** and **13** give the same C_{MWNT} (within experimental error) as in 0.6 M NaCl. This suggests that the two cations have essentially the same effect on PEG linker surfactants, unlike C6 linker surfactants. We conclude that the interaction between the ether oxygen atoms and the alkali metal cations is not affected by hydration enthalpy to the same extent as that between amide oxygen atoms and cations.

Attempts to disperse MWNTs in 0.3 M $CaCl_2$ using both **1** and **3** resulted in no observable dispersion.[§] However, for **9** and **13** C_{MWNT} values of 12 ± 1 mg L^{-1} (4%) and 3 ± 1 mg L^{-1} (1%) respectively, were obtained. These are very low levels compared to DI water, 0.6 M NaCl or 0.6 M KCl. To see if the negative effect of calcium ions could be overcome, the ability of **13** to disperse MWNTs in a mixed solution of NaCl and $CaCl_2$ was investigated. We chose **13** because this surfactant afforded a higher C_{MWNT} in 0.6 M NaCl than DI water (Figure 3). A solution that was 0.3 M in NaCl and 0.15 M in $CaCl_2$ was used to maintain the overall charge density. The resulting low C_{MWNT} of 14 ± 0 mg L^{-1} (4%) was only slightly higher than in 0.3 M $CaCl_2$. We conclude that the formation of poorly soluble calcium carboxylates explains the negative effect of calcium ions on C_{MWNT} (although it was possible to prepare 1 mM surfactant solutions in this medium without observing precipitate formation).[¶]

Stimulus Responsive Behaviour

Sensitivity to pH was expected in all of our surfactants. At low pH the carboxylate groups will be converted to less hydrophilic carboxylic acids, which should impact on the stability of MWNT dispersions. We investigated this effect using HCl and surfactants which had little sensitivity to NaCl, namely **4** and **9**. This would ensure that any response was related to the change in pH and not the formation of NaCl (salt formation from protonating the carboxylate groups and subsequent acid-base additions). Dispersions of MWNTs prepared using **4** and **9** in both DI water and 0.6 M NaCl were therefore tested for a pH response.

Neat MWNT-surfactant dispersions (Figures 6a and 6b) were divided into three 0.5 ml aliquots. In each case, two of these were treated with 25 μL of 1 M HCl solution (the third was used as a control) and the samples were left overnight under ambient conditions. This is an excess of acid compared to the surfactant carboxylate groups (*ca.* 17 or 50 equivalents for **4** and **9**, respectively) which ensures the dispersion is at an acidic pH. The addition of acid increased the dispersion volume by 5%, but dilution has no effect on dispersion stability. In all cases the formation of a black precipitate was observed in the acid-treated samples (Figure 6c), with no change to the untreated control sample. One of the acid-treated samples was then neutralised with 25 μL of 1 M NaOH (again increasing the dispersion volume by 5% relative to the initial 0.5 ml). Gentle agitation of the neutralised sample by hand-held swirling for only 2 seconds was sufficient to re-disperse the precipitate (Figure 6d), which remained stable for more than 1 week. When the remaining acid-treated samples dispersed using **9** were agitated in the same way it was possible to re-suspend the precipitate; however in this case it re-formed within *ca.* 90 min (Figure 6e). We also observed that addition of an equivalent amount of 1 M HCl to a solution of **9** in DI water caused the solution to become cloudy (Figure 6f). Phase separation occurred slowly over *ca.* 7 h. This surfactant is therefore insoluble in acidic media (this was exploited in the purification of intermediate G0 acids by acid-base workup – see the Experimental Section in the SI).

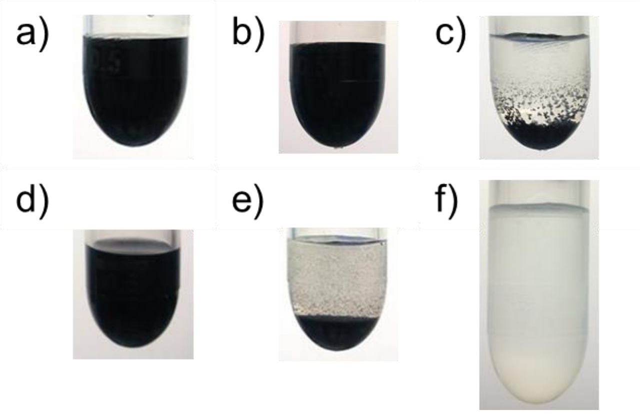

Fig 6 Photographs of MWNT dispersions and surfactant solution at various stages of the acid and base treatment process: a) Dispersion **A**: MWNTs in 1 mM **9** in DI water; b) Dispersion **B**: MWNTs in 1 mM **9** in 0.6 M NaCl; c) acid-treated **B** after standing overnight under ambient conditions; d) acid-treated **B** 6.5 h after neutralisation and gentle agitation; e) acid-treated **A** 1.5 h after re-suspending the precipitate which formed on standing overnight by gentle agitation; f) 1 mM **9** in DI water after addition of HCl.

These results demonstrate that a *reversible* response has been induced in dispersions of MWNTs using our carboxylate surfactants. We rationalise this behaviour as follows: addition of acid converts the carboxylate moieties into carboxylic acids, eliminating their ionic character. This means there is no longer any Coulombic repulsion between functionalised MWNTs. Furthermore, the acid form of the surfactants is insoluble in acidic, aqueous media. The functionalised MWNTs are now hydrophobic, causing them to aggregate and precipitate. The ease with which a stable dispersion can be re-formed following neutralisation is indicative that the surfactant remains bound to the MWNT surface throughout the process. If precipitation occurred due to stripping of the surfactant from the MWNT surface, the unfunctionalised MWNTs would be expected to re-form bundles bound by strong van der Waals and π-π interactions, which would require ultrasonication to re-disperse. Treatment with base converts the carboxylic acids back to carboxylate salts, restoring their ionic character. The functionalised MWNTs again repel one another through Coulombic interactions and are sufficiently hydrophilic to be dispersed in aqueous media. Re-dispersion is facile as the precipitated, functionalised MWNTs are much more weakly bound than pristine MWNT bundles. This mechanism is illustrated in Figure 7. Our results are comparable with those reported by Ikeda *et al.* for SWNTs dispersed initially in basic solution using folic acid.[44]

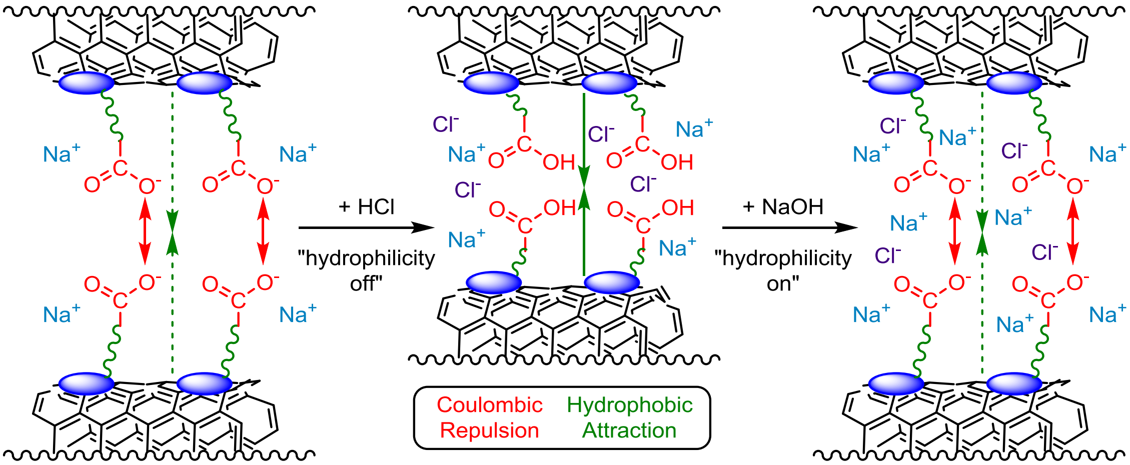

Fig 7 Proposed mechanism of acid-base triggered reversible dispersion of MWNTs. For clarity a SWNT is shown to represent a MWNT surface, and a G0 surfactant is shown schematically.

Simulations

In order to better understand the observed trends along surfactant series, simulations were carried out on the series PyrB-PEGn-CH_2COONa for n = 2, 4, 6, 8, 12 (i.e. surfactants **7, 8, 9** and **10** and an additional n = 8 analogue). The calculations showed that the solvation energy ΔE_S (kcal mol^{-1}) as a function of PEG chain length followed similar trends to the experimentally determined C_{MWNT} in both DI water and 0.6 M NaCl (Figure 8).

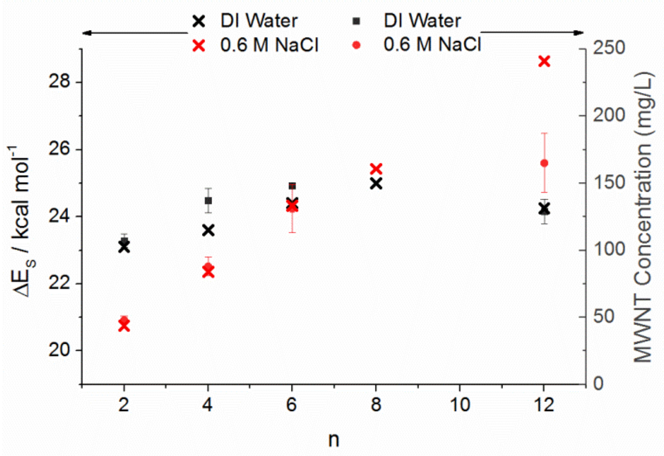

Fig 8 Comparison of the trends in calculated ΔE_S (crosses, left y-axis) and experimentally determined C_{MWNT} (faded data points, right y-axis) with increasing n for surfactants of general structure **PyrB-PEGn-CH$_2$COONa** (e.g. **7-10**). Results are shown for both DI water (black) and 0.6 M NaCl (red). The relative positions of the y-axes are arbitrary, and were selected to highlight the similarities between the observed trends.

The solvation energies of the surfactants were calculated using the molecular dynamics package AMBER13.[45] A number of uncorrelated snapshots of the simulation (which involves long production run times in excess of 5 ns) were collected and Molecular Mechanics Generalised Born Surface Area (MMGBSA) post processing was then performed. The MMGBSA method[46] uses topology files to extract the molecule at each snapshot and applies the Generalised Born Surface Area (GBSA) approximation to simulate the effects of the polar solvent (either water or 0.6 M NaCl) at that particular conformation. The whole series of results yields the Gibbs free energy ΔG at each simulation time step. This mean force potential approximation averages out the degrees of freedom of the solvent molecules (so they are often referred to as implicit solvents) and allows computation of solvent-mediated interactions. The Gibbs free energy is defined by $\Delta G(p,T) = \Delta H - T\Delta S$ where ΔH is the enthalpy and ΔS the entropy. As a first approximation we ignore the entropic contribution and follow the MMGBSA method and define $\Delta G_{mmgbsa} = \Delta H$ for small volume changes upon mixing.

In an implicit water (salt solution) model using molecular dynamics there are several contributions to ΔG_{mmgbsa} which are defined as follows. The non-polar contribution to ΔG_{vdw} includes a term related to the solvent accessible surface area SASA. The parameters are extracted from experiment[47] for small PEG chains, $\Delta G_{nonpolar} = SASA*0.00542 + 0.92$ kcal/mol, whereas ΔG_{polar} corrects ΔG_{coul} by including the active Born radius of an atom embedded in the molecule to adjust for screening effects. These contributions are summed to give

$$\Delta G_{mmgbsa} = \Delta G_{vdw} + \Delta G_{coul} + \Delta G_{polar} + \Delta G_{nonpolar}$$

The solvation energy is then defined by

$$\Delta E_S = \Delta G_{mmgbsa} - \Delta G_{mmgbsa,vacuum} .$$

For both the calculated ΔE_S and experimental C_{MWNT} it is observed that a shorter PEG linker (lower n) gives higher values in DI water than in 0.6 M NaCl, but the rate of increase with n is larger in the latter case. For each property the DI and 0.6 M NaCl results are comparable for n = 6 (surfactant **9**). In DI water, the calculated decrease in ΔE_S between n = 8 and n = 12 parallels the lower C_{MWNT} of surfactant **10** (n = 12) compared to **9** (n = 6). The approximately linear increase in ΔE_S with n in 0.6 M NaCl throughout the investigated range contrasts the trend in C_{MWNT}, which initially appears linear but shows a much smaller increase from n = 6 (**9**) to n = 12 (**10**). Nonetheless, the data indicate that ΔE_S could be a suitable property on which to base at least qualitative predictions of the ability of surfactants to disperse MWNTs. This is reasonable as higher solvation energy is indicative of increased solvent miscibility which would be expected to result in improved CNT dispersion.

Conclusions

New surfactants based on a pyrene anchoring unit, amide (C6) or ether (PEG) linker, and a (multi-)carboxylate (G0, G1, or G2) head group have been synthesised and their ability to disperse MWNTs in aqueous media, including salt solutions, has been examined and compared with commercial surfactants and linker-free analogues. In Millipore (DI) water the PEG linker surfactants disperse MWNTs at least as well as commonly used commercial anionic surfactants under our standard, unoptimised conditions. They are also more effective than comparable linker-free and C6 linker surfactants. The ability of surfactants to disperse MWNTs appears to relate to several factors, including linker type and length, the charge density of functionalised MWNTs, surfactant packing efficiency,[21] ionic screening effects and surfactant-ion interactions. A combination of these effects means that surfactants can show increased, decreased or similar levels of MWNT dispersion in 0.6 M NaCl solution relative to DI water. This effect is primarily dependent on surfactant structure; for example, a longer OEG linker results in improved MWNT dispersion in 0.6 M NaCl. The effect of other salts was briefly examined: KCl was found to have a similar effect to NaCl for PEG linker surfactants, but resulted in higher dispersion concentrations for C6 linker surfactants. $CaCl_2$ resulted in very low dispersion levels for all of the materials tested, which we propose is due to the formation of poorly soluble calcium carboxylates. We have also demonstrated a pH response in MWNT dispersions prepared using a PEG linker or C6 linker surfactant. Addition of HCl resulted in precipitation of MWNTs which could be reversed by addition of an equivalent quantity of NaOH. Furthermore, theoretical studies showed that the ability of a surfactant to disperse MWNTs in aqueous media can be related to its solvation energy ΔE_S. It would be of future interest to see if comparable effects can be observed in dispersions in organic media.

Overall, we have established that the nature of the linker unit used to connect the aromatic anchoring moiety and hydrophilic head group of a surfactant can have a considerable impact on its ability to disperse MWNTs. This represents a significant advance in the design of molecules for this purpose.

Acknowledgements

We thank BP Exploration Operating Company Ltd for funding and Dr Budhika Mendis for the TEM data.

Notes and references

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Electronic Supplementary Information (ESI) available: Experimental details for molecular synthesis and characterisation; copies of NMR spectra; analytical procedures. See DOI: 10.1039/b000000x/

* These are Sodium Dodecyl Sulphate (SDS), Sodium Dodecyl Benzenesulphonate (SDBS), Sodium Cholate (SC), Sodium Deoxycholate (SDOC), Sodium Pyrenebuytrate (SPB), (the sodium salt of commercial 1-pyrenebutyric acid), and Triton X-100.

† The small error associated with ε is not included in the data as it is smaller than the standard deviation.

‡ i.e. a 0.6 M concentration of chloride ions and an overall 0.6 M ‘concentration’ of positive charge. Note that this does not represent the same ionic strength (or Debye length) as the 0.6 M NaCl and KCl solutions due to the higher contribution of multivalent ions to this parameter.

§ Based on these results dispersion was not attempted using **4**.

¶ Another contributing factor could be the slightly reduced Debye length of 0.3 M $CaCl_2$ compared to 0.6 M NaCl and KCl (0.321 nm vs. 0.392 nm) which would result in an increased ionic screening effect. In (at least) the case of the surfactants with amide moieties it is also noteworthy that the hydration enthalpy of calcium ions is considerably larger than that of sodium and potassium ions, potentially making cation-amide interactions much less favourable.

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