A Universal Ultracentrifuge Spectrometer Visualizes CNT–Intercalant–Surfactant Complexes

Engin Karabudak,^[a] Claudia Backes,^[b] Frank Hauke,^[b] Cordula D. Schmidt,^[b] Helmut Cölfen,^[c] Andreas Hirsch,^[b] and Wendel Wohlleben^{*,[a]}

Interacting solutes form multiple associates and usually mask each other in ensemble characterization. They are susceptible to preparation artefacts in the single-molecule techniques commonly applied. To overcome the problem of bulk characterization of a single-walled carbon nanotube (CNT) dispersion with a novel surfactant–intercalant mixture, we obtain color movies of fractionation under extreme gravity, such that each colloidal component is characterized independently. We combine the unique fractionation power of ultracentrifugation^[1] with full absorption spectra $c(\lambda)$ at each radial position r at each time step t during the sedimentation process.^[2,3] In ref. [8], ligand attachment CNTs was studied with the Beckman model XLA centrifuge, which tracks only $c(r,t)$ at a single wavelength, requiring extended modeling for analysis. Our spectrometer/CCD optics^[2,3] adds a third dimension and generates wavelength-resolved movies of the centrifuge fractionation $c(r,t,\lambda)$. This allows independent ligand and CNT tracking without hydrodynamic modeling. We identify the interactions in unpurified intercalant–surfactant–CNT dispersions and obtain the unexpected proof of four coexisting heteroassociates by a novel model-free evaluation.

Solubilization of carbon nanotubes is of primary importance to increase the processability of this unique class of materials. Despite the progress in separating and sorting SWCNTs by electrophoresis, density gradient ultracentrifugation or chromatography, CNT-based technology has not yet been realized on a commercial scale, as the CNT separation is limited to individualized nanotubes.^[4,5] It has previously been shown that designed water-soluble perylene bisimide derivatives such as **1** are excellent CNT surfactants, yielding CNT dispersions with up to 73 % of the CNTs stably dispersed and containing 60 % of in-

dividualized nanotubes.^[6,7] Since the designed perylene-based surfactants are rather large molecules that cannot easily slip between adjacent nanotubes in CNT bundles during the ultrasonication induced unzipping, we have extended the dispersion concept herein by the use of perylene tetracarboxylic acid dianhydride (PTCDA) as an intercalant. PTCDA should exhibit a high affinity to the CNTs, as it also possesses the perylene moiety as anchoring group to the aromatic nanotube scaffold. Since PTCDA does not carry bulky substituents in the periphery, it should enhance nanotube exfoliation during sonication. The nanotube bundles should thus be more efficiently broken up and the individual nanotubes can then be stabilized by surfactant **1**. Dispersions have been prepared by immersing PTCDA and HiPco CNTs (0.1 g L⁻¹) in a buffered aqueous solution of the perylene surfactant **1** (phosphate, pH 7).

The mixture was sonicated (30 min in a bath-type sonicator) and mildly centrifuged (15 krpm, 30 min) in order to remove coarse aggregates such as insoluble PTCDA and large CNT bundles. After centrifugation, the concentration of CNTs in the supernatant was calculated from the optical density (OD) of the absorption spectra and the corresponding CNT extinction coefficient^[6] (Table S1, Supporting Information) after dilution of the dispersion (1:1 with the corresponding buffered aqueous solution of **1**). The dispersion efficiency, for example, the concentration of CNTs in the supernatant after centrifugation was increased in the presence of PTCDA, however no additional peaks attributed to PTCDA were detected in the absorption spectra (Figure S1a, Supporting Information). As it has previously been shown that the amount of stably dispersed CNTs can be increased at higher pHs, the procedure was repeated in a pH 10 buffer (borate).^[6] Again, the dispersion efficiency of the perylene surfactant was significantly enhanced by addition of PTCDA (Table S1, Supporting Information).

The efficacy of this surfactant system is underlined by the fact that 88 % of the starting material remains in the supernatant after precentrifugation for CNT-**1**-PTCDA (2:3:2) at pH 10. In the absorption spectra for pH 7 and pH 10 dispersions, no relative changes in the absorption peaks associated with the excitonic transitions of the CNTs are observed (Figure S1, Supporting Information). However, the ratio of the perylene to CNT absorption intensity is changed upon the addition of PTCDA. For example, the relative intensity of the perylene **1** transitions at 500 nm and 550 nm decreases with respect to the CNT absorbance. This indicates that the perylene surfactant **1** is partly removed from the supernatant solutions, as it may form aggregates with the insoluble bulk PTCDA added in excess. Based on these observations, it is tempting to assume that the intercalant PTCDA and **1** strongly interact by π - π

[a] Dr. E. Karabudak, Dr. W. Wohlleben
Polymer Physics Research
BASF SE, 67056 Ludwigshafen (Germany)
Fax: (+49) 621 6092281
E-mail: wendel.wohlleben@basf.com

[b] C. Backes, Dr. F. Hauke, C. D. Schmidt, Prof. Dr. A. Hirsch
Department of Chemistry and Pharmacy
and
Institute of Advanced Materials and Processes (ZMP),
University of Erlangen-Nuremberg
91054 Erlangen (Germany)

[c] Prof. Dr. H. Cölfen
Department of Physical Chemistry
University of Konstanz
78457 Konstanz (Germany)

[*] These authors contributed equally.

stacking interaction resulting in 1) the precipitation of 1 together with PTCDA and concomitantly 2) the solubilization of PTCDA.

Presumably, the CNTs are encapsulated by the surfactant, as indicated by the perylene transitions (see Figure S1, Supporting Information), so that their characteristic absorption profiles should sediment with equal speeds. However, the role of the intercalant cannot easily be extracted from steady-state absorption. For example, it is unclear whether the intercalant PTCDA is part of the same structure. But is PTCDA truly solubilized by the surfactant? And would it not be more convincing to observe such interactions directly?

In order to elucidate the complex interactions in the three-component mixture, we applied band sedimentation in a multiwavelength Analytical Ultracentrifuge (MWL AUC), essentially a spectrometer/CCD synchronized to centrifugal fractionation. The process, raw data and evaluation results are summarized in Figure 1. The CNT dispersion was placed in the sample reservoir of a vinograd cell. These cells open a small capillary when the pressure rises during the increasing centrifugal acceleration. This leads to the overlaying of the sample (in H₂O) onto the solvent column of higher density (in this case a 1:1 mixture

of H₂O and D₂O) at a radial position of 6.33 cm. Data acquisition started as soon as the final rotational frequency of 55 000 rpm was reached and continued for 78 min, generating 131 snapshots of the fractionation process with radial step size 50 μ m and 45 s intervals. The movie Band55_1.avi (Supporting Information) reviews the one-hour experiment in a few seconds and perfectly visualizes the fractionation of fast and slowly sedimenting colloids with very distinct absorption profiles. One of the snapshots from this movie is shown in Figure 1c, where we define radial Range 1 for the fast-moving colloids which sedimented after 7 min already half way to the bottom of the cell on the right. Radial Range 2 defines the slowly sedimenting colloids.

In order to extract the absorption profiles of the different components, which will allow attribution to molecular interactions, we chose individual snapshots and integrated the absorption $c(r, \lambda)$ over the radial ranges $[r]$ as indicated. The fast-moving colloids are best captured at the very beginning (first minute, Figure 1b). We define Range 1a (6.5 cm to 6.8 cm) with the integrated absorption profile in Figure 1e. This profile is characteristic for the main fraction of the dispersion, namely individualized CNTs encapsulated by the perylene surfactant 1

Figure 1. Process, raw data and evaluation of wavelength-resolved band sedimentation. a) Initial absorption of the CNT dispersion, of which 15 μ L are layered onto the solvent during speed-up of the centrifugal force, which acts in the radial direction. Repeated snapshots of $c(r, \lambda)$ are acquired by fast radial scanning of a spectrometer; b) snapshot at the 1st minute, where only fast-moving colloids are visible, evaluated as Ranges 1a and 1b; c) snapshot at the 7th minute, where the fractionation of fast (Range 1) and slow (Range 2) sedimenting colloids with their distinct absorption profiles is best visualized; d) snapshot at the 78th minute, where a substructure within the slow colloids appears, evaluated as Ranges 2a and 2b; e)–h) integration of the ranges, attributed to e) individualized CNT with attached surfactant and f) CNT bundles with few surfactant molecules attached, g) hydrolyzed intercalant, h) intercalant–surfactant micelles. Movies of this experiment are in the Supporting Information.

with its 0 $\rightarrow$ 1 transition at 500 nm and its 0 $\rightarrow$ 0 transition at 550 nm, respectively. However, there is also a second range, Range 1b, with colloids that sedimented faster than the individualized CNTs (6.8 to 7.1 cm). Their absorption profile (Figure 1 f) contains comparatively less surfactant, attributed to the decrease of accessible surface area in CNT bundles.

The absorption profiles of the slowly sedimenting colloids extracted from the last scan (78th minute, Figure 1 d; Movie Band55_2.avi, Supporting Information) visualize that also the slowly sedimenting colloids are composed of two discrete fractions. One fraction with an absorption peak at 500 nm does sediment (6.55 to 7.1 cm, range 2b), but another fraction without that absorption component (6.3 to 6.55 cm, Range 2a) virtually stands still except for some diffusional broadening. The absorption profile of Range 2b (Figure 1 h) contains the typical absorption peaks of the perylene surfactant **1** and is hence attributed to surfactant micelles. We note that from this measurement, one can determine the quantity of surfactant adsorbed on the CNT surface.

But there is also the rather unexpected, but very distinct component of the non-sedimenting Range 2a. Its absorption profile (Figure 1 g) contains only the peaks of the intercalant PTCDA, with vanishing traces of **1**. The observation that the absorbance peaks at 438 nm and 465 nm that may originally be attributed to PTCDA correspond to a molecule neither associated with perylene surfactant micelles, nor with the sedimenting CNTs, strongly suggests that this species is not the PTCDA intercalant, as PTCDA is highly self-aggregating and not water-soluble without stabilization. We propose that under the basic conditions employed in the experiment (buffer pH 10), the anhydride functionalities are opened to yield the corresponding perylene tetracarboxylic acid (PTC). We suggest that PTCDA is initially acting as intercalant during the sonication-induced exfoliation of the nanotubes. During the sonication process PTCDA comes in contact with the nanotube surface where it is intermittently adsorbed by π - π stacking interaction. As PTCDA is a rather small molecule compared to surfactant **1**, it may also slip between the adjacent nanotubes in large bundles, thereby increasing the amount of stably dispersed CNT material. For the pH 7 dispersions, where no traces of PTCDA have been detected in the stable CNT dispersions, the PTCDA intercalant is presumably replaced by **1**, resulting in re-aggregation with the remaining bulk PTCDA and thus sedimentation during precentrifugation. In the case of the pH 10 dispersions, the PTCDA is exposed to the basic environment while being adsorbed on the nanotube where it is hydrolyzed to yield perylene tetracarboxylic acid. (For results on the hydrolysis with independent methods, compare the Supporting Information) Since the experiment is carried out under basic conditions, the carboxylic acid groups of PTC are deprotonated and thus negatively charged. In contrast to surfactant **1**, the charges are located directly next to the aromatic unit (peryene moiety) serving as anchoring group to the CNTs so that the π - π stacking interaction is no longer ensured, resulting in desorption of the PTC.

Note that for the success of our experiment, the choice of solvent density ($H_2O:D_2O=1:1$) facilitated the near-complete

separation of components, whose sedimentation coefficients^[1] were far apart with ~ 100 Svedberg (Sved), 15 Sved, 0.6 Sved, <0.1 Sved for Ranges 1b, 1a, 2b and 2a respectively. This justifies simply integrating spatial ranges for the extraction of absorption profiles. This model-free evaluation can be extended with spectral shape analysis of each fraction, to quantify compositions. Furthermore, the data acquired is open for hydrodynamic evaluation at specific wavelengths, via the anhydrous specific volume and shape factor to the ligand density on the colloidal surface.^[8] An even more elaborate evaluation would take advantage of the full absorption spectra, to extract absorption profiles in correlation with sedimentation coefficients for each colloidal component. An obvious advantage is the enhanced statistical relevance, because the entire movie $c(r,t,\lambda)$ instead of a selected snapshot $c(r,\lambda)$ is evaluated. In fact, such an elaborate evaluation of MWL data is under development in the Ultrascan^[9] evaluation platform, but it is not yet available as shareware. However, similar to the global evaluation of AUC data with respect to frictional ratios,^[9] supercomputer facilities will be required. It would then be possible to apply our techniques to systems with colloidal components whose sedimentation coefficients differ only slightly or to simplify from band to homogeneous sedimentation as well.

In summary, we have dispersed CNTs by a highly efficient two-component surfactant system, but with unknown interactions and complex absorption spectrum (Figure 1 a). In a single measurement with the MWL AUC, we visualized the existence of distinct components (Band55_1.avi, Supporting Information) and extracted their absorption profiles (Figures 1 e–h). We provided evidence (also from alternative methods, see the Supporting Information) that PTCDA is hydrolyzed after executing its role as intercalant. We suggest that PTCDA is adsorbed on the CNT by π - π stacking interaction only intermittently. As PTCDA is a rather small molecule, it may slip between the adjacent CNTs in large bundles, therefore assisting exfoliation and increasing the amount of stably dispersed CNT material. When exposed to a basic environment, the PTCDA is hydrolyzed while being adsorbed on the CNT to yield the perylene tetracarboxylic acid, which in turn desorbs from the CNT surface. By the use of a unique centrifuge spectrometer recording the entire UV/Vis absorption during fractionation of $\sim 10^{10}$ colloids, this complex CNT dispersion could be analyzed in a single experiment. Beyond the present application, MWL band sedimentation with model-free spectral integration can be applied to any light-absorbing solution or suspension, including hetero-associating proteins and antibodies, semiconductor and metal colloids, and their functionalizing ligands.

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